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CONTENTS

THE DEVELOPMENT OF SUPERCONDUCTIVITY IN OXIDES

K. Alex Müller

IBM Research Division, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

Starting with the first observation of superconductivity in an oxide, the history of its development is traced. Basically, and consecutively, three kinds of oxide superconductors have been found: Transition metal lons with small coulomb on-site repulsion, U, oxides with cations exhibiting charge disproportionation, and finally the cuprates with large Hubbard U.
This discussion will lead over to a characterization of the highest-T_c materials, both concerning their physical properties and application perspectives.

FABRICATION AND CHARACTERIZATION OF BSCCO FILMS

Keiichi Ogawa, Keikichi Nakamura, Hirotoshi Hayakawa*, Hisao Hattori** and Shozo Ikeda

National Research Institute for Metals, Tsukuba Japan, *Yaskawa Electric Mfg. Co. Ltd., Kitakyusyu Japan, **Sumitomo Electric Industries, Ltd., Itami Japan

Since the dicovery of a series of high Tc superconducting oxides, many attempts have been made to fabricate these oxide films. Various kinds of physical (ie, MBE, sputtering and laser ablation) as well as chemical vapor deposition technique were exploited. The present state of the fabrication technique will be briefly reviewed, focusing on the 110K mono-phasic film of BSCCO compounds. Main difficulties arise from the following reasons: 1)Easy intergrowth, 2)Complex atomic arrangement in the Bi-O double layers, 3)Manipulation of chemically similar elements Ca and Sr and 4)Multicomponent system (ie, as many as five components).

To overcome these difficulties, we fabricated the 110K mono-phasic film by the following two methods. 1) We initially fabricate the amorphous BSCCO film with the correct stoichiometry by sputtering and subsequently anneal the resultant amorphous film at a controlled Pb potential to transform it exclusively into the 110K phase. 2) We fabricate Bi-O/Sr-Ca-Cu-O multilayered films using the two target reactive magnetron sputtering technique and subsequently cool the film in an oxygen atmosphere. The substrate temperature was kept at 665°C. The film shows superconductivity without being post annealed. Details of the characterization and superconducting properties of these films will be reported at the ISS'89.

MAGLEV TRAINS

Shunsuke Fujiwara
Railway Technical Research Institute
2-8-38 Hikari-cho Kokubunji-shi Tokyo, 185 Japan

Maglev vehicle has superconducting coils composed of niobium-titanium alloy wire. The superconducting coils are exposed to various magnetic or mechanical environments, when they are used to generate propulsion, levitation and guidance forces simultaneously. They must support those forces and moments of three directions. And the harmonic magnetic field generated from the guideway coils is larger than that of the usual rotary machine, because the arrangement of the guideway coils is simplified. Then the effects of this harmonics must be understood well. The outline of the superconducting magnet, linear synchronous motor and the levitation system will be explained. Then the electromagnetic forces acting on the coil sides which are generated by linear synchronous motor or levitation system will be investigated.

HETERO EPITAXIAL GROWTH MECHANISM OF THIN FILM FOR HIGH-Tc SUPERCONDUCTORS

Takahito Terashima, Kenji Iijima*, Kazunuki Yamamoto*, Kazuto Hirata*, Katsuhiko Hayashi* and Yoshichika Bando

*Institute for Chemical Research, Kyoto University, Uji 611, Japan
*Research Institute for Production Development, Shimogamo-Morimoto-cho 15, Sakyo-ku, Kyoto-shi 606, Japan

Initial stage of the epitaxial growth and growing manner of the copper oxide superconductors (Y-Ba-Cu-O, Nd-Ce-Cu-O, La-Ba-Cu-O) thin films on the $SrTiO_3$(100) and MgO(100) were investigated by means of in situ reflection high energy electron diffraction (RHEED) and X-ray diffraction. In situ RHEED observation showed that the formation of the perovskite structure occured even at initial deposit and the growth manner was layer by layer. Crystal structure of the ultrathin (<100Å) films were strongly affected by the lattice mismatch between the substrate and film. When the Y-Ba-Cu-O (001) film was grown on the MgO(100) with the large mismatch of 9%, RHEED observation revealed that the initial deposit kept the same in-plane lattice spacing as MgO and the lattice spacing converted from the bulk value of MgO to that of Y-Ba-Cu-O when the layer became thicker than 12 Å. X-ray analysis of the 100 Å thick film on the MgO(100) showed that the film had the orthorhombic symmetry. Whereas, 100 Å thick Y-Ba-Cu-O film on the $SrTiO_3$(100) had the tetragonal symmetry induced by the misfit strain because of the small lattice mismatch of 2%. Both 100 Å thick films on MgO(100) and $SrTiO_3$(100) showed the superconducting transition at 80K. The dependence of the superconductivity on the film thickness will be reported.

THIN FILM OF HIGH-Tc SUPERCONDUCTOR

H. Itozaki and S. Yazu

Itami Research Laboratories, Sumitomo Electric Ind., Ltd.

1-1 Koyakita 1-Chome, Itami, Hyogo, 664, Japan

High Tc superconducting thin films were developed by a sputtering method. REBaCuO, BiSrCaCuO and TlBaCaCuO thin films show a high critical current density (Jc) at 77.3K. Their Jc is more than 3MA/cm2 at 77.3K in a zero magnetic field. Pinning force was evaluated by measurement of magnetization creep or by analysis of the resistivity-temperature curve near the superconducting transition. Activation energy of pinning is not significantly different from those of sintered materials. High Jc films are stronger against a magnetic field than poly-crystal films or sintered bulk materials, because grain boundaries act as barriers or weak links for a supercurrent. Therefore, the high Jc of the thin film might be explained by a much higher density of pinning centers or by the effect of the grain boundary.

Microwave propagation was measured by a Network Analyzer. Microwaves of up to 10GHz can pass through a superconducting line (0.5umDx100umWx12mmL) with losses of less than 0.3dB per 12mm. This is much smaller than those of aluminum line at 77.3K. This indicates that high Tc materials can be used to make high frequency transmission lines in high speed devices or their packages. Josephson junctions are another potential application of such films. We tried to create one with a YBCO/Au/YBCO structure. The appearance of weak constant voltage steps when micro waves are irradiated suggests that Josephson junctions can be made by this thin film process.

HETERO-EPITAXIAL GROWTH OF YBaCuO THIN FILMS

Takeshi KOBAYASHI and Masahiro IYORI

Department of Electrical Engineering, Faculty of Engineering Science
Osaka University, Toyonaka, Osaka 560, Japan

The double hetero-epitaxial growth of $Y_1Ba_2Cu_3O_y/MgO/Y_1Ba_2Cu_3O_y$ system and its application to the new superconductivity electronics will be demonstrated. The films were grown by the conventional reactive magnetron sputtering method. So far, narrow success has been obtained in preparation of the epitaxial double heterostructures of stacked HTSC and insulating layers. The varieties of the structure are (001)YBCO/(100)MgO/(100)YBCO, (110)YBCO/(~100)MgO/(110)YBCO and (001)YBCO/(100)MgO/(001)YBCO. The thickness of the intermediate MgO layer ranges from 1 to 20 nm. The crystallinity of the film was checked by RHEED, XRD and cross-sectional TEM observations.

Using this technique, the electric field effect device like an MOS diode was fabricated. It revealed a capacitance variation against the gate voltage application in accordance with a p-type MOS theory.

THIN FILM, OMCVD PROCESS FOR HIGH-Tc SUPERCONDUCTIVITY

Hitoshi Abe
Research Laboratory Oki Electric Industry Co.,Ltd.
550-5, Higashiasakawa-cho, Hachioji-shi, Tokyo 193

At the beginning of 1988, high-Tc ceramic thin films have been successfully prepared by the organo-metallic chemical vapor deposition (OMCVD) method. Within less than one year Y-Ba-Cu-O films could be prepared with a quality of Tc higher than 90K and Jc = $1.9 \times 10^6 A/cm^2$ at 77K, which is comparable to that obtained by sputtering or MBE method. However, more than 800°C had been still required for the formation temperature, while other methods required much lower formation temperature.

Very recently, by using of N_2O gas instead of O_2 gas as an oxygen source, Y-Ba-Cu-O superconducting films could be prepared on various substrates at 650°C without post annealing process. The electrical quality of films became poorer in the series of $SrTiO_3$(100), MgO(100) and Si(100) substrates. Deposition rate of Y-Ba-Cu-O films on MgO(100) substrates by using N_2O was nearly one half of that using O_2. In this invited talk, the potentiality of the OMCVD method for a high-Tc thin film formation technique is reported.

HIGH-Tc SUPERCONDUCTING FILMS PREPARED BY CVD

Hisanori YAMANE, *Hideyuki KUROSAWA, Akira SUHARA, Toshio HIRAI,
Kazuo WATANABE, Hideo IWASAKI, Norio KOBAYASHI and Yoshio MUTO

Institute for Materials Research, Tohoku University
2-1-1 Katahira Aoba-ku, Sendai 980, Japan
*RIKEN Co., 810 Kumagaya, Kumagaya 360, Japan

Y-Ba-Cu-O(YBCO) superconducting films were prepared on $SrTiO_3$ (100) single crystal substrates at 850°C by chemical vapor deposition(CVD) and in-situ oxygen treatment. The source materials used were 2,2,6,6-tetramethyl-3,5-heptanedionates (thd:$C_{11}H_{19}O_2$) of yttrium ($Y(thd)_3$), barium ($Ba(thd)_2$) and copper ($Cu(thd)_2$).

X-ray diffraction patterns of the films indicated that the films consisted of mostly c-axis oriented grains with a few of a-axis oriented grains.

Superconducting transition temperature defined by zero resistivity was up to 92 K. The highest transport critical current density(Jc) at 77 K and 0 T was $2x10^6$ A/cm^2. Jc above 10^4 A/cm^2 at 77 K was measured even in a magnetic field of 27 T applied parallel to the substrates and perpendicular to current.

The composition ratios of Y, Ba and Cu of the films were determined by ICP spectroscopy. The films having Jc above 10^5 A/cm^2 at 77 K and 0 T exhibited higher copper ratios compared to Y:Ba:Cu=1:2:3.

Needle-like and granular grains were observed at surfaces of the films by scanning electron microscopy. EDX analysis revealed that granular projections had higher copper content than matrix of the films. The composition of needle-like grains were almost the same as that of matrix. The needle-like grains seemed to be a-axis oriented YBCO.

TAILORED SUPERCONDUCTING THIN FILMS PREPARED BY LAYER-BY-LAYER DEPOSITION

Tomoji KAWAI, The Institute of Scientific and Industrial Research,
Osaka University, Mihogaoka, Ibaraki, Osaka, 567 Japan

Layer-by-layer successive deposition is one of the most promising methods to fabricate "Tailored Superconducting Films". The numbers of CuO_2 layers, the distance between the layers and carrier concentration of Bi-Sr-Ca-Cu-O superconductors have been artificially controlled to alter the superconductive properties using this technique with laser ablation. Bi(Pb)-Sr-Ca-Cu-O films containing one to five CuO_2 layers between Bi_2O_2 have been fabricated around 500C under N_2O atmosphere. The Bi atom in the Bi_2O_2 has been site-selectively substituted by Pb to control the superconductivity. Using this technique, control of the composition in the atomic layer scale has also been possible by incorporating atoms and ions of different ionic radii into the crystal structure. Site-selective substitution of Ba for Sr or Ca has been performed.

PREPARATION AND CHARACTERISTICS OF $Nd_{2-x}Ce_xCuO_4$ THIN FILMS

S.HAYASHI,K.HIROCHI,H.ADACHI,S.KOHIKI,S.HATTA,K.SETSUNE,T.HIRAO and K.WASA
Central Research Laboratories,Matsushita Electric Industrial Co. Ltd.,
Yagumo-nakamachi 3-15,Moriguchi,Osaka 570,Japan

Characteristics of the electron-doped-type $Nd_{2-x}Ce_xCuO_4$ system have been systematically studied using the high quality thin films. The $Nd_{2-x}Ce_xCuO_4$ thin films with various Ce concentrations, x, have been prepared by rf magnetron sputtering and subsequent annealing. The films showed a highly oriented structure with the c axis normal to the substrates. By means of the reducing treatment (annealing in a vacuum), superconductivity was induced for the films with $0.14<x<0.18$. The superconducting and transport properties of the films were highly affected by the reducing treatment. The $x=0.15$ film exhibited a sharp superconducting transition with zero resistivity at 22 K, in consistent with the diamagnetic properties. The resistivity of the film was fairly low with metallic characteristics, and the sign of the Hall coefficient was negative in the normal state. On the other hand, the normal-state optical measurements showed that the undoped Nd_2CuO_4 is a semiconductor with a charge transfer gap of 1.3 eV, and that, when Ce ions were doped, a plasma reflection due to the free-carriers came to be seen with the plasma frequency of 1.07 eV for $0.14<x<0.18$. Moreover, x-ray photoemission study revealed that the Cu valence of the film decreased from 2+ for x=0 to 1+ for x=0.15. The physical properties revealed here are in contrast with those of hole-doped-type cuprate superconductors, and will be useful for the investigation of the nature of electron-doped superconductivity.

CHARACTERIZATION of SUPERCONDUCTING OXIDE THIN FILMS by X-RAY DIFFRACTION

T. IWATA, Y. ENOMOTO, S. KUBO, K. MORIWAKI and A. YAMAJI
NTT Opto-electronics Laboratories
Tokai, Ibaraki, 319-11, Japan

It is difficult to characterize the structure of thin films. Electron diffraction methods such as RHEED gives us information of the structure of thin films, but, it is only about their surfaces. The X-ray diffraction method gives information about the internal structure of the films. Conventional X-ray diffraction gives us only information from a plane parallel to the substrate. In this study, we characterized a structure of $YBa_2Cu_3O_y$ thin films by X-ray diffractometer with a 4-circle goniometer to obtain information from a plane not parallel to the substrate.

Sample films were deposited onto $SrTiO_3$ substrates by rf-sputtering or co-evaporation. The $YBa_2Cu_3O_y$ films deposited on $SrTiO_3$ (110) substrates have two preferred orientations, (110) and (103). To identify this preferred orientation, the (102) diffraction peak was measured because it is not masked by the diffraction from the substrate. Semi-quantitative analysis was carried out to evaluate the ratio of (110) and (103) domains. Intensity data was corrected by using data from the Si standard to correct for χ angle dependence. The films in which the RHEED method had detected only the (110) domain revealed a large amount of (103) domain. The results indicate that the films grow both (110) and (103) directions at the first stage of deposition and they grow only in the (110) direction in the second stage. The ratio of (110) and (103) domains varies with its growth conditions. Even if the films contain two preferred orientation domains, the growth directions of the films are well correlated with the direction of the substrates. These results indicate that the characterization of the structure inside the films is important. We believe that the X-ray diffraction method is much more useful than the electron diffraction method for characterizing the film's internal structure. To characterize the structure of the films, both methods are needed.

DIRECTIONAL SOLIDIFICATION PROCESSING OF HIGH T_c SUPERCONDUCTING OXIDES

Y. SHIOHARA, M.NAKAGAWA, T.SUGA, K.ISHIGE, T.OYAMA, T.IZUMI, S. NAGAYA, M. MIYAJIMA, I. HIRABAYASHI, AND S. TANAKA
Superconductivity Research Laboratory, ISTEC, Tokyo, JAPAN

Unidirectional solidification processing, including Floating Zone Melting, Laser Zone Melting, and Vertical Bridgman methods for making high T_c superconducting oxides has been investigated. The potential importance of solidification processing route was revealed by the high critical current densities demonstrated by S. Jin *et al.* and M. Murakami *et al.*, in textured $YBa_2Cu_3O_{7-X}$.

In this presentation, we show the effects of processing parameters on texture, morphology, grain size, and structures of unidirectionally. grown crystals. Processing parameters include growth rate (R), temperature gradient (G), specimen size (d), and initial composition (C_o). Strongly aligned structures were obtained at a high G/R ratio. The grains grown unidirectionally become larger and longer with decreasing a growth rate (R). The interrelation between the superconducting characteristics and textured structure produced will also be discussed.

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BENEFICIAL EFFECT OF USING 211 FOR THE FORMATION OF 123 SUPERCONDUCTING PHASE

Hyungsik Chung, Hae-Doo Kim, Jaewoong Koh

Korea Institute of Machinery and Metals, Changwon Korea

The superconducting $YBa_2Cu_3O_{7-x}$(123 Phase) is mostly synthesized by solid state reaction through repeated calcining and sintering. In this case, the full decomposition of $BaCO_3$ is difficult since the calcining and sintering are performed generally at temperatures below 1000°C to avoid liquid phase formation. This can be partially responsible for the low sintered denisty and low Jc commonly observed in the sintered compact.

The present work shows that utilizing the intermediate $Y_2Ba_1Cu_1O_5$(211 phase) as the base material for synthesizing the 123 phase can raise the processing temperature and improve the sintered properties significantly. In addition, the 123 phase grown from 211 phase shows better development of (001) plane, implying that better grain alignment to(ab)plane can be obtained by this process.

The grain alignment is explained by the crystal orientationship between the orthorhombic 211 and 123 structure.

CONTACT RESISTANCE AND PROXIMITY EFFECT OF YBCO/Ag INTERFACE

Koichi Mizushima, Hiroshi Kubota and Jiro Yoshida
Advanced Research Laboratory, Research and Development Center, Toshiba Corporation
1, Komukai Toshiba-cho, Saiwai-ku, Kawasaki, 210, Japan

Good electric contact to YBCO films can be achieved by evaporation and subsequent heat treatment of silver (or noble metals). However, proximity effect to silver and Josephson current through YBCO/Ag/S (conventional superconductor) junction have not been well established. Nonlinear current-voltage characteristic observed for a YBCO/Ag/PbO_x/Pb junction has been difficult to be attributed to quasiparticle tunneling between superconducting silver and lead because of the weak temperature dependence at low voltages.

We present a direct evidence of superconducting current through a YBCO/Ag/Pb junction. Partition of supercurrent between the junction and a parallel superconducting wire was detected by using a zero input-resistance galvanometer which was made of Nb-Ti wire and solder bob (Clark element). Critical current of the junction depended much on the sample and ranged from 10 mA/mm^2 down to less than 10 $\mu A/mm^2$ which was the detection limit of the apparatus. Below the critical current, flux conservation phenomenon was observed for the above superconducting loop composed of the junction, the galvanometer and the superconducting wire.

ELECTROMAGNETIC PROPERTIES AND STRUCTURES OF BiPbSrCaCuO SUPERCONDUCTING WIRES

Ken-ichi Sato, Takeshi Hikata, Hidehito Mukai and Hajime Hitotsuyanagi
Osaka Research Laboratories,Sumitomo Electric Industries, Ltd.
1-1-3 Shimaya, Konohana-ku, Osaka, 554 Japan

BiPbSrCaCuO superconducting wires were fabricated through the powder in silver sheath method. The maximum transport current density at 77.3 K in a zero magnetic field was over 2×10^4 A/cm^2. Zero resistivity temperature of these wires was 106 K. The magnetic field dependence of Jc (0.1μV/cm criterion) was summarized as follows for the magnetic field direction parallel to a-b plane: 7,250 A/cm^2 at 0.1 Tesla, 1,540 A/cm^2 at 1 Tesla and 240 A/cm^2 at 2 Tesla.

A highly textured structure was observed with c-axis of the high-Tc phase perpendicular to the longitudinal direction of the flat wires through XRD, SEM and TEM. Fine dispersion of non-superconducting phases, such as CaSrPbO and SrCaCuO, was observed along c-planes. Intergrowth of low-Tc phases was also observed frequently. Jc-B properties showed that these structures can be expected to act as the pinning sites.

50 cm length, 150 amperes class cable was first made of 20 strands of 0.5 mm thickness flat wires. This cable was tested in liquid nitrogen and confirmed carrying critical current of 150 A with a criterion of 1μV (10^{-12} Ω·m in resistivity). This data shows the potential of high-Tc wires for low-field application, such as cables and power-leads, in the first stage.

THE TRANSPORT CRITICAL CURRENT PROPERTY OF HIGH Tc SUPER-CONDUCTING WIRES.

Naoki Uno, Noritsugu Enomoto, Hiroyuki Kikuchi and Kaname Matsumoto

The Furukawa Electric Co., Ltd. Yokohama, 220 Japan

The Ag sheathed high Tc superconducting wires were prepared by the powder-in-tube method. The trasport critical current density(Jc) was measured by the four-probe method. And the magnetic dependence of transport Jc at various temperatures were evaluated. In YBCO system, we obtained the Jc of 10^3A/cm^{2}order, but we could not obtain the higer Jc because of the weak link problem. The flux pinning mechanism of YBCO superconductor using melt process was evaluated with measuring the magnetic field dependence of transport Jc. In case of BSCCO system, the Ag sheathed wires showed strong grain alignment which could be attained by rolling and adjusting the condition of heat treatment. So we obtained the Jc of 10^4A/cm^{2}order But this Jc decreased drastically under high magnetic field over 1 T, because of the problem of the weak pinning force and the large flux creep. We also studied the microstructure and super-normal transition of these Ag sheathed wires.

The authors gratefully acknowledge that this work was supported by the group of Tokyo Electric Power Company, Tohoku Electric Power Company Hokkaido Electric Power Company and Electric Power Development Co., Ltd.

TWO DIMENSIONAL PHASE FLUCTUATION IN HIGH-T_c SUPERCONDUCTOR UNDER THE MAGNETIC FIELD

Masashi BAN, Tsuneo ICHIGUCHI, Toshiyuki ONOGI† and Toshiyuki AIDA

Central Research Laboratory, Hitachi Ltd., Tokyo 185, Japan
†Advanced Research Laboratory, Hitachi Ltd., Tokyo 185, Japan

The resistance $R(=V/I)$ of high-T_c superconducting $ErBa_2Cu_3O_{7-x}$ film (T_c=87K) is measured as a function of current I and magnetic field H at temperatures T below T_c. It has been found, in the magnetic field parallel to c-axis, that both I-V and H-V characteristics are represented by power laws in the forms of $V \propto I^{n(T,H)}$ and $V \propto H^{m(T,I)}$ and that the Nelson-Kosterlitz jump in the exponents n and m is observed at the temperature where n=3 and m=2, respectively. These behaviors are explained by the Kosterlitz-Thouless transition caused by thermally excited vortex-antivortex pairs on the two dimensional CuO_2 planes. Even in the magnetic field with an arbitrary angle to c-axis, the two power laws are observed. The induced voltage V depends on the angle, while the exponents n and m remain unchanged when the angle varies even though the magnetic field is parallel to CuO_2 planes. For any direction of the magnetic field, the thermally excited vortex-antivortex pairs reduce the critical current J_c of high-T_c superconductor to zero.

STRUCTURAL AND PHYSICAL PROPERTIES OF Ca SUBSTITUTED $YBa_2Cu_4O_8$

N.KOSHIZUKA, T.MIYATAKE, K.YAMAGUCHI, R.ITTI, S.GOTOH, and S.TANAKA

Superconductivity Research Laboratory, ISTEC, Shinonome 1-10-13, Tokyo 135, JAPAN

The 80K superconductor $YBa_2Cu_4O_8$ which contains double Cu-O chains is stable for the oxygen content up to high temperature (~850°C). A superconductive transition of ~90K is achieved by substitution of Ca for Y in $YBa_2Cu_4O_8$.

In this review, the structural and physical properties of $Y_{1-x}Ca_xBa_2Cu_4O_8$ (x =0, 0.02, 0.05, 0.1) examined by X-ray diffraction, high-resolution transmission electron microscopy, electric resistivity, magnetization and photoelectron spectroscopy measurements are presented. The polycrystalline samples are prepared by solid state reaction with O_2-HIP treatments. There are no impurity phase peaks in the X-ray diffraction patterns of $YBa_2Cu_4O_8$ samples, however, HRTEM measurements revéal that they have planer defects with $YBa_2Cu_3O_7$ and $Y_2Ba_4Cu_7O_{15}$ like structures. Electric resistivity and magnetic susceptibility vs. temperature measurements show that Tc increases with Ca content. The increase of Tc seems to be due to the increase in the electron hole concentration per a Cu-O plane. The photoelectron spectra demonstrates the existence of Fermi edge like structure in $YBa_2Cu_4O_8$ at room temperature. Ca substitution effects on the superconducting properties such as Hc, ξ , and λ are also discussed in comparison with those of $YBa_2Cu_3O_7$.

TRANSPORT AND MAGNETIC PROPERTIES IN Tl-SYSTEM SUPERCONDUCTORS SHOWING LARGE T_c-VARIATIONS

Yoshimi Kubo, Yuich Shimakawa, Takashi Manako and Hitoshi Igarashi
Fundamental Research Laboratories, NEC Corporation
4-1-1 Miyazaki, Miyamae-ku, Kawasaki 213, Japan

We have found that large T_c-variations often observed in Tl-system superconductors were due to very small change in oxygen content. In a series of compounds $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$, variations in T_c were 0K-85K, 85K-110K and 116K-110K for $n=1$, 2 and 3, respectively. Here, the former T_c values were for samples annealed in oxygen at ~350°C, and the latter values were for samples annealed in argon at ~550°C. The oxygen contents for argon-annealed samples were less than those for oxygen-annealed samples by 0.10~0.15 per formula unit. Both Hall coefficient (positive) and normal resistivity were increased by argon-annealing, which indicated that the hole concentration was decreased by the oxygen deficiency.

Since both hole concentration and T_c are easily controlled by slightly changing the oxygen content, these systems are good models for the study of hole doping and superconductivity. In particular, the $n=1$ system, which contains a Cu-O octahedron layer between Tl_2O_2 layers, provides a novel example which varies from a 85-K superconductor to a metallic nonsuperconductor without significant structural change, as the hole concentration increases. Details of transport and magnetic properties in these systems will be reported.

Y. Shimakawa et al., Physica C 157(1989)279.
Y. Kubo et al., Proc. of M^2S-HTSC, July, 1989, Stanford.

STRUCTURE AND SUPERCONDUCTING PROPERTIES OF $[(Ln_{1-x}Ln^*_x)_{1/2}(Ba_{1-y}Sr_y)_{1/3}Ce_{1/6}]_8Cu_6O_z$

H. Yamauchi, T. Wada, A. Ichinose, Y. Yaegashi, T. Kaneko, S. Ikegawa and S. Tanaka

Superconductivity Research Laboratory,
International Superconductivity Technology Center,
10-13 Shinonome 1-Chome, Koto-ku, Tokyo 135 Japan

A variety of new oxide superconductors that can be represented by the formula, $[(Ln_{1-x}Ln^*_x)_{1/2}(Ba_{1-y}Sr_y)_{1/3}Ce_{1/6}]_8Cu_6O_z$ (Ln, Ln* = lanthanide elements), have been prepared. The crystallographic structures of the oxides were all tetragonal and of the $(Ln^+,Ce)_4(Ln^+,Ba)_4Cu_6O_z$ (Ln^+ = Nd, Sm or Eu) type which had been previously discovered by Akimitsu et al. As the Sr content, y, increased when Ln=Ln*=Nd, the oxygen content, z, monotonically increased and the superconducting transition temperature, T_c, varied exhibiting a maximum. When z was controlled directly by means of high oxygen pressure sintering techniques, T_c was changed accordingly. T_c's of samples with differnt combinations of Ln and Ln* and differnt values of x and y were found to depend on the magnitude of the bond valence sum for a Cu atom located in the bottom plane of the Cu-O_5 piramid. Transport and magnetization measurements were carried out to investigate the magnetic field dependence of superconducting properties and to determine the phenomenological parameters. The Hall coefficients were positive below room temperature and varied yielding a maximum with respect to temperature.

SINGLE CRYSTAL OF HIGH-Tc SUPERCONDUCTOR.

Yoshikazu Hidaka
NTT Laboratories, 162 Tokai, Ibaraki, 319-11, Japan

Copper oxide superconductors of various kinds have been discovered in recent years. The measured values of the physical properties of these compounds continue to be upgraded by the use of improved samples. Thus at this stage of high-Tc study, it should be stressed that the production of well-characterized high quality materials is fundamental for understanding high temperature superconductivity. Despite the novel two-dimensional magnetic features found in flux grown crystals, their superconducting properties are still inferior to those of ceramic samples. For YBCO and LSCO, crucible contamination even at very low concentrations(<1%) has an effect on physical properties. Tc is suppressed and some defects are created in the structure by these impurities. Pt and Al which substitute for Cu, affect electronic transport in the CuO two-dimensional planes. Consequently, the choice of crucible is very important in the prevention of contamination. And further we must develop a contamination-free growth method for high Tc cuprate compounds. In this context, the growth of high-Tc cuprate single crystals is reviewed emphasizing the contamination effects on physical properties especially in flux grown crystals.

SYNTHESIS AND PROPERTIES OF SINGLE Cu-O LAYER COMPOUNDS

Y. TOKURA

Department of Physics, University of Tokyo, Tokyo 113, Japan

Several families of copper oxide compounds with different shapes of Cu-O single layers have been synthesized to invesitgate electronic structures and properties characteristic of High T_c compounds. Optical studies on the single crystal speciemens have revealed charge-transfer gaps and spin exchange energies dependent on the Cu-O networks. Doping-induced changes in electronic structures are discussed together with electronic phase diagrams of three represcntative single CuO_2-layer systems -T, T^* and T' phases-.

X-RAY ABSORPTION NEAR-EDGE STUDIES OF $Nd_{2-x}Ce_xCuO_{4-y}$

H. Oyanagi, H. Yamaguchi, Y. Yokoyama, T. Katayama and Y. Nishihara
Electrotechnical Laboratory, Umezono, Tsukuba-shi, Ibaraki 305, Japan

The effect of electron doping and annealing under reducing conditions on the electron states at the copper sites in $Nd_{2-x}Ce_xCuO_{4-y}$ (x=0.15) has been systematically studied by X-ray absorption near-edge structure. We find that the absorption edge of Nd_2CuO_4 shifts to lower energy upon Ce^{4+} doping, indicating the reduction of Cu valence. Comparison of the difference spectra using Nd_2CuO_4 as a standard further confirmed that doped electrons partially occupy Cu d-holes forming Cu^+ (d^{10}) species. The effect of annealing under reducing conditions was studied for a series of samples with different oxygen pressures (pO_2=1-10^{-4} atm). It is demonstrated that annealing under reducing conditions enhances the Cu valence reduction, which is strongly correlated with electrical and superconducting properties.

MEISSNER SIGNAL OF SINGLE CRYSTAL, POLYCRYSTAL AND POWDER SPECIMENS OF OXIDES

Authors; Koichi Kitazawa, Osamu Nakamura[A], Tetsuya Hasegawa, Teruo Matsushita[B], Isao Tanaka[C], Hironao Kojima[C], Hiromi Takei[D] and Masato Murakami[E]

University of Tokyo, Tokyo; Tonen Corp., Ohi-machi,Saitama[A]; Kyushu University, Fukuoka[B]; Yamanashi University, Kofu[C]; Sumitomo Electric Ind, Osaka[D]; SRL, Tokyo[E];

Abstract

Field cooling curves were compared on various oxides ; LSCO, YBCO, BSCCO and TlBCCO in various forms under various magnetic fields. It has been concluded that the Meissner fraction is strongly dependent on the field and the sample size: increasing with decrease in field as well as with decrease in the sample size. This results in the smaller observed meissner fraction in singlecrystal specimens than in powder ones under the commonly employed magnetic fields. The polycrystalline samples behave like singlecrystals in the low field range, but like powders in the high field range due to the presence of the grain boundaries. A new model is presented by assuming the flux exclusion process from the specimen surface against the pinning force which is gradually intensified as T decreases. In a large size specimen, the flux exclusion occurs only in the vicinity of the surface. This is the reason why larger singlecrystalline specimens give smaller meissner fraction. In the case of polycrystalline specimens, the flux exclusion proceeds via the grain boundary regions, thereby leading to a larger Meissner fraction than in single crystal but to a smaller fraction than in powders.

RESISTIVE STATE OF HIGH TEMPERATURE SUPERCONDUCTORS IN MAGNETIC FIELDS

Y. Iye, S. Nakamura, T. Tamegai, T. Terashima*, K. Yamamoto* and Y. Bando*

The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106 Japan
** Institute for Chemical Research, Kyoto University, Uji, Kyoto 611 Japan*

The resistive transition of high temperature superconductors (HTSCs) is not only important in contemplating potential applications of the HTSCs, but is also very rich in fundamental physics problems. When the experiments are conducted using high quality single crystals or epitaxial films, the angular dependence of the phenomenon reflects such vital issues as anisotropy of superconductivity. Our recent magnetotransport studies using epitaxial $YBa_2Cu_3O_{7-y}$ films have revealed the anisotropy not only with respect to the c-axis but also within the ab-plane. Also central in the phenomenon is the flux dynamics. Our experimental results suggests that the Lorentz driving force for the fluxes becomes important in a higher current density regime, but the behavior in the low current Ohmic regime seem to require a more sophisticated model. An interesting feature suggestive of flux pinning at twin boundaries has been observed.

Magnetotransport experiments above T_c will be also reported and discussed in terms of superconducting fluctuation effect. The HTSCs offer a unique opportunity to study the superconductin fluctuation effect on the Hall conductivity.

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FLUX PINNING MECHANISM AND CRITICAL CURRENT DENSITY IN HIGH-TEMPERATURE SUPERCONDUCTORS

T. Matsushita
Department of Electronics, Kyushu University,
Fukuoka 812, Japan

Flux pinning strength and resultant critical current density in high-temperature superconductors are argued by comparing with those in ordinary low-temperature superconductors.

The elementary pinning force by planar defects such as twinning planes in YBaCuO or grain boundaries in Nb_3Sn is proportional to $B_c^2\xi/2\mu_0$, where B_c is the thermodynamic critical field and ξ is the coherence length. This value in YBaCuO at 77 K is samller by a factor of about 3 than that in Nb_3Sn at 4.2 K. In addition, the thermal energy at 77 K is larger by a factor of 18 than that at 4.2 K. Hence, the effect of thermally activated flux creep is significant when YBaCuO is used at 77 K.

One issue of the significant flux creep is that the critical current density is reduced to zero above a certain magnetic field, called irreversibility field. This field can be increased to sufficiently high values for application by introducing strong pinning centers of high concentration. The other issue is that the persisitent current decays gradually with time. Unfortunately, this decay is considered to be notable at 77 K in high fields, even if we succeed to increase the pinning strength up to a theoretical limit.

FLUX CREEP OF MELT PROCESSED $YBa_2Cu_3O_7$

M. Murakami, H. Fujimoto, S. Gotoh, N. Koshizuka, and S. Tanaka
Superconductivity Research Laboratory,
International Superconductivity Technology Center,
1-10-13, Shinonome, Koto-ku, Tokyo 135 Japan

Giant flux creep is considered to be a serious problem for large scale applications of oxide superconductors at liquid nitrogen temperature. A combination of low pinning energy and large thermal energy is believed to cause large flux creep. However, the pinning energy can be increased by introducing effective pinning centers, therefore giant flux creep is not inherent to oxide superconductors.

In this paper, we show that large pinning energy about two orders of magnitudes larger than that of single crystals, can be obtained in melt processed YBaCuO superconductors. We also show that the pinning energy varies depending on the microstructure of the samples. This result indicates that we need to control microstructure in order to improve the pinning energy.

APPLICATION OF SUPERCONDUCTIVITY FOR POWER SYSTEMS

Y. AIYAMA
Electrotechnical Laboratory
1-1-4 Umezono, Tsukuba-shi, Ibaraki 305, Japan

The applications of the superconductor (SC) technologies to the electric power supply system are mainly discussed with emphasis on their meaning to the system.

The final goal is to realize the totally SC-rized power system, which have the highes efficiency, power density, stability, availability and reliability. Though the conventional huge systems exist already, replacing a conventional apparatus in the system with the SC one should be the first step toward the goal, obliging it to have the same rated specifications as the conventional one. At the progressed stage of SC-rizing the system, the optimum rated conditions will be able, e.g., shares of the electric power by the rated voltage vs. the current of the system, shares of the output by the electric vs. magnetic loadings of the apparatus, etc. In introducing SC apparatuses into the system, not only their higher efficiencies but also their higher economic gains, their more advanced performances or their new functions in the system are required, compared with conventional ones.

A synchronous generator with SC field windings, the economical and technical feasibility of which can be foreseen, is the first target of the MITI/AIST/ML Project, started in FY 1988. The technical requirements and problems are reviewed.

SC cables, transformers, energy shortages, etc. are under the feasibility study by ISTEC:MITI/ANRE. E.g., SC cables are estimated to be feasible economically with their transmission capacity over 5GVA(LHe)/3GVA (LN_2), being beyond ones in the present system. The more efforts or ideas to reduce a cable-core cost are necessary. In the SC power system, power electronics will be also important.

POWER SYSTEM CONTROL EXPERIMENTS USING 1MJ SMES

HIDEKI FUJITA
Chubu Electric Power Co.,Ltd.
Nagoya,Japan

Superconducting magnetic energy storage (SMES) system is considered to be useful in electrical power system because of high efficiency and quick response This is an attractive technology for load leveling and system stabilization in electrical utility.

Chubu Electric Power Co.,Ltd. and Hitachi,Ltd.have been studying SMES since 1988 and developed 1MJ SMES composed of pulsed superconducting magnet (1000A,2H) and tested its basic characteristic in this August.In this paper,we report on this system and several plans and results of power control experiments connecting this system to the simulated power system which contains generators, transmission lines and fluctuating load.

DEVELOPMENT OF SUPERCONDUCTING LINEAR INDUCTION MOTOR

O. Tsukamoto*, Y. Tanaka**, K. Oishi***, T. Kataoka*** and Y. Yoneyama***
* Faculty of Eng. Yokohama Nat'l Univ., Yokohama, Japan, ** Furukawa Electric Co., Yokohama, Japan,
*** Nippon Steel Co., Kitakyushu, Japan

We have developed superconducting linear induction motor (SLIM) using ultra fine filament NbTi AC superconductor. The superconducting primary windings, 3-phase and dipole, are 15cm long and 7cm wide and put in liquid helium. The dia meter of the filament of the AC superconductor is 0.5μm. The secondary conductor is a metal plate placed in the room temprature region. Generaly, AC superconductors are highly unstable and easily quenched by a frictional heating caused by a wire motion of only a few μm. To prevent the windings from prematur quench caused by conductor motions, they are epoxy-impregnated. The SLIM was tested by applying 3-phase 50Hz AC current and the maximum input was 5.5kW at 360A (effective value). Measured torque was 5.3g at 310A (effective value) with a copper plate as the secondary conductor.

HIGH-TC OXIDE SUPERCONDUCTING MAGNET WITH AN IRON CORE

Toshie Ushijima, Shoichi Yokoyama, Kenji Shimohata,
and Tadatoshi Yamada
Central Research Laboratory, Mitsubishi Electric Corp., Amagasaki,
Japan 661

High-Tc oxide superconducting magnet with an iron core was developed. It is possible to make up the closed circuit of persistent current by using high-Tc oxide superconductors.

The magnet has an iron core, an induction coil and 15 pieces of $YBa_2Cu_3O_{7-y}$ rings (OD26.2mm , ID21.2mm , t2mm). The iron core has an air gap of 2mm to measure the magnetic field. Five rings were sintered at the same time. One ring in each sintering was cut in half, and the critical current was measured by the four-probe method. The critical current was about 8A (at 77K, 0T). The persistent currents of $YBa_2Cu_3O_{7-y}$ rings were induced by induction coil.

The magnetic field in the air gap measured by hall device was about 1.5 kGauss. The persistent current passing into a $YBa_2Cu_3O_{7-y}$ ring estimated from the field strength was about 8A. It was in agreement with the critical current measured by the four-probe method.

PROXIMITY EFFECT IN THE SYSTEM OF Y-Ba-Cu-O/Au/Nb FILMS

HIROSHI AKOH

Electrotechnical Laboratory
1-1-4 Umezono, Tsukuba, Ibaraki 305, Japan

The proximity effect between high-T_c superconductors and normal metals is very important to understand the surface properties of high-T_c superconductors, since this effect reflects electronic properties of high-T_c superconductors, such as a short and anisotropic coherence length, surface superconductivity, and so forth. An *SNS* (superconductor-normal metal-superconductor) junction is one of the typical examples to investigate the proximity effect, since the junction clearly shows the Josephson effect which gives us the information of the contact between high-T_c superconductors and normal metals. This junction also has a potential application as high-T_c superconducting devices. In this paper, we present the proximity effect in *SNS* Josephson junctions with film-layered structures, which consist of Y-Ba-Cu-O/Au/Nb film sandwiches.

Superconducting films of Y-Ba-Cu-O with smooth surfaces were fabricated by an rf diode sputtering method with post-deposition annealing and by a reactive coevaporation method without annealing. In order to improve the surface superconductivity of Y-Ba-Cu-O films, O_2 plasma treatment was carried out with a high pressure of O_2 and a low rf power before the deposition of Au barrier. The junctions reveal Shapiro steps under microwave radiation, according to the ac-Josephson effect. Magnetic field dependence of the critical current shows a Fraunhofer pattern with the self-field effect, indicating that the junction size is larger than the Josephson penetration depth. We have studied the temperature dependence of the critical current, which shows that the thickness of Au barrier is shorter than the coherence length of Au. Moreover, the relationship between the proximity effect and crystalline orientation of films will be discussed.

THREE-TERMINAL DEVICES OF HIGH-TC SUPERCONDUCTORS

Hidetaka Higashino, Kentaro Setsune and Kiyotaka Wasa

Matsushita Electric Industrial Co., Ltd.
Moriguchi, Osaka, Japan

The study of three terminal devices using high-Tc superconductors is paid much attention. At present, difficulties still lie on the fabrication technology of high-Tc tunnel junctions. Although promising types of the three-terminal devices are at present bridge ones having various control means, junction type devices should be more intensively studied. In this paper, two types of high-Tc three terminal devices for basic studies are introduced.

One is a variable critical-current Josephson junctions (VCJJ). The VCJJ comprises a high-Tc superconducting thin film, which has a 10μm wide bridge shape, a Ta_2O_5 buffer layer and a Ta heater. The heater has an arched shape of 10 μm width and 2μm in length, on the center of the bridge. The heating current generates a temperature distribution in the superconducting film. Therefore, the superconducting current path is made narrower beneath the arch and a weak link Josephson junction characteristics are trimmed.

The other type of three-terminal device is a current injection type Josephson junction with dual Al gates using a Bi-Sr-Ca-Cu-O superconducting thin film. The gate current (Ig) was injected to/extracted from the film through the two gates which were deposited on the film with a narrow gap. The critical current of 2.5 mA with zero Ig was suppressed down to 1.0 mA by applying Ig of 0.3 mA and the differential current gain of 7.9 near zero Ig was achieved at 4.2 K. The device has a possibility of high speed operation.

FABRICATION OF DC SQUID WITH AS-GROWN YBaCuO THIN FILM BY FOCUSED ION BEAM

Masami Tanioku, Ken'ichi Kuroda, Kazuyoshi Kojima, Koichi Hamanaka, Yasushi. H. Hisaoka†, Akira Shuhara†, and Hidenobu Murakami†

Central Research Laboratory, †Manufacturing Development Laboratory, Mitsubishi Electric Corporation, Tsukaguchi, Amagasaki, 661 Japan

We fabricated a dc superconducting quantum interference device (SQUID) with an as-grown YBaCuO thin film of 50 nm thickness, which was deposited on a MgO(100) substrate by RF magnetron sputtering from three targets. This film has a very smooth surface and a highly textured c-axis perpendicular to the substrate surface. In the patterning process the implantation technique with a focused ion beam (FIB) was successfully employed to fabricate Josephson microbridges from the as-grown thin film.

Several pairs of microbridges of same widths ranging from 1 to 3 μm were drawn by scanning the FIB of 80 keV Ga^+ with a dose of 10^{16} ions/cm^2. Then the pattern of the SQUIDs with loop areas of 40 μm by 10 μm was defined by photolithography and chemical etching process. The microbridges with widths of 1.5, 2.0, 2.5, and 3.0 μm indicated the superconducting transition; the microbridge width for the transition is limited due to the crystal damage caused by the ions distributed in the periphery of the FIB beam spot of 0.2 μm in diameter. The devices respond to the micowave of 15 GHz and show Shapiro steps. Furthermore, the quantum interference effect was observed appreciably with the device constructed of the 1.5 μm-width microbridges under the applied magnetic field at 8 K. The observed noise of the SQUID originated mostly from the pre-amplifier at high frequencies.

MICROWAVE PROPAGATION ON HIGH-Jc YBCO TRANSMISSION LINES

K. HIGAKI, S. TANAKA, H. ITOZAKI and S. YAZU

Itami Research Laboratories, Sumitomo Electric Ind., Ltd.

1-1, Koyakita 1-Chome, Itami, Hyogo, 664 Japan

We have prepared YBCO superconducting transmission lines on the substrates of a MgO single crystal by RF magnetron sputtering and chemical wet etching. We have studied the propagation of microwave signals from 130MHz to 20GHz on these lines. The transmission lines are co-planar type and are 0.5um thick, 100um wide, and 12mm long. They are spaced 35um from the ground planes on both sides. Both ends of the line are patterned 1mm wide in order to contact the line with the connectors.

The temperature dependence of the resistivities and the critical current densities were directly measured through the whole line (12mm long) by a four-probe method in a cryostat. Tc of The line was 87K and its Jc was 4×10^5 A/cm^2 at 77.3K.

The transmission and reflection characteristics of the YBCO superconducting co-planar lines were measured by a network analyzer at 77.3K. The results were compared with those of Al transmission lines. The transmission losses on the YBCO co-planar line were less than 0.3dB for frequencies up to 10GHz and less than 1.5dB for frequencies up to 16GHz. They are lower than those on the equivalent Al line on a MgO single crystal at 77.3K. This indicates that a YBCO superconducting transmission line has lower attenuation and lower dispersion than an Al line and YBCO can be superior chip-to-chip or board-to-board interconnections to normal metals.

TAPERED TUBE LENSES FOR INTENSE ELECTRON BEAMS (SUPERTRONS)

H. Matsuzawa, Y. Ishibashi, T. Osada, and T. Akitsu
Yamanashi University, Kofu 400, Japan

We previously proposed lenses (Supertrons) for intense electron beams (relativistic electron beams, 310 keV, 1 to 3 kA in peak value with pulse width less than 5 ns) and demonstrated their potential with Y- and Bi-based high-Tc superconductor tubes [1-4]. The lenses were composed of funnel-type inlets and straight tubes (inner diams of 20, 10, and 5 mm, and axial lengths of 25 to 30 mm). The tubes were damaged, during the experiments, on the corner from the funnel inlets to the straight tubes when the inner diams were narrow (10 and 5 mm).

In the present paper, we used Bi-based superconductor lenses which were composed of funnel inlets and tapered tubes. The exits of the tapered tubes were 5 and 10 mm in diam. The corner from the funnel to the tapered tubes was 20 mm in diam because no damage was observed in the previous experiments for the lenses with that diam. For comparison, copper made lenses were used which had almost the same dimensions as those of the superconductor lenses.

The tapered lenses focused higher electron beam currents in thinner foci than the straight tube lenses did, and no damage was found on the corners. There would exist optimized configuration of the lenses.

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CARRIER DOPING AND SUPERCONDUCTIVITY OF LAYERED COPPER OXIDE.

HITOSHI NOBUMASA[*], KAZUHARU SHIMIZU[*], MASATAKA TANAKA[**], YUKISHIGE KITANO[**] AND TOMOJI KAWAI[***]

[*]Composite Material Lab.,Toray Ind.Inc.,2-1,Sonoyama 3-chome,Otsu,Shiga,520

[**]Toray Research Center Inc.,1-1,Sonoyama 1-chome,Otsu,Shiga,520

[***]The Institute of Scientific and Industrial Research,Osaka University, Ibaraki,Osaka,567

The possibilities of making new or improving superconducting materials were studied by doping carriers into an insulating oxide or a superconducting oxide, which contain plural $Cu-O_2$ planes in an unit cell.

The carrier control in $La_2Sr_1Cu_2O_{6-y}$, La_2CuO_4 and $LaSrCuO_4$ were carried out for studying the appearance of superconducting properties of layered copper oxide. Two methods were adopted for carrier doping ; the first was changing the sintering conditions and the second was F doping.

The relationships between crystal structure or oxygen content and superconducting properties were investigated by partial substitution of Sr for Ba and high oxygen pressure treatment, for $(Nd_{1/3}Ba_{2/3})_2(Ce_{1/3}Nd_{2/3})_2Cu_3O_y$ superconductor which contains three $Cu-O_2$ planes in an unit cell. Tc_{zero} of this superconductc which was annealed under 1300 atm oxygen pressure at 600 ℃ for 24 hours, were 4 K and the volume fraction was larger than 40 % according to the Meissner signal at 4.2 K.

We intend to report the superconducting properties of these materials related to some physical parameters in detail.

PREPARATION AND CHARACTERIZATION OF $(La,Ln,Ba,Sr,Ce)_8Cu_6O_Z$ (Ln:Nd,Sm,Eu,Gd,Dy,Ho,Er,Tm,Yb and Y) CERAMICS

Y. Yaegashi, T. Wada, A. Ichinose and H. Yamauchi

Superconductivity Research Laboratory,
International Superconductivity Technology Center,
10-13 Shinonome 1-Chome, Koto-ku, Tokyo 135, Japan

Ceramic samples of $[La_{1/6}Ln_{1/3}Ce_{1/6}Ba_{1/6}Sr_{1/6}]_8Cu_6O_Z$ (Ln : Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Y) have been prepared. The samples for Ln = Nd, Sm, Eu, Gd and Dy exhibited superconductivity while those for Ln = Ho, Er, Tm, Yb and Y were non-superconductors. The highest superconducting transition temperature of 34 K was obtained for Ln = Eu and Gd. Samples were prepared employing a standard solid state reaction method and annealed at 1020 °C in 3 atm oxygen pressure atmosphere. X-ray diffraction patterns indicated that they were of single phase or nearly single phase. The crystal structures were all tetragonal and of the $(Eu,Ce)_4(Eu,Ba)_4Cu_6O_{Z_8}$ type, and the lattice parameters were : a ~ 3.8 Å and c ~ 28.4 Å. As the atomic number of the rare earth element, Ln, increased from 63(Eu) to 67(Ho) both lattice parameters, a and c, decreased, and as the atomic number of Ln increased from 67(Ho) to 69(Tm) both lattice parameters increased: the lattice parameters for the samples with Ln = Ho were the smallest. The temperature dependence of resistivity and ac magnetic susceptibility were measured. It was found that samples with Ln = Nd, Sm, Eu, Gd and Dy were superconducting having T_c's = 20-35 K.

90K SUPERCONDUCTIVITY IN Ca-SUBSTITUTED $YBa_2Cu_4O_8$

T.Miyatake, K.Yamaguchi, T.Takata, S.Gotoh, N.Koshizuka and S.Tanaka

Superconductivity Research Laboratory, International Superconductivity Technology Center, Tokyo 135, Japan

$YBa_2Cu_4O_8$ has an excellent thermal stability in oxygen content up to higher temperatures compared with $YBa_2Cu_3O_7$. This feature may be important for practical applications. However, the lower Tc of 80K in $YBa_2Cu_4O_8$ cannot lead to uses at liq. N_2 temperature. In this work, we describe the increase to 90K in Tc with Ca substitution in $YBa_2Cu_4O_8$.

Samples of $Y_{1-x}Ca_xBa_2Cu_4O_8$ (x=0.0-0.1) were prepared by a high oxygen pressure technique employing Hot Isostatic Pressing in ($Ar+20\%O_2$) gas environment. X-ray diffraction data showed that each sample had the $YBa_2Cu_4O_8$ structure with no $YBa_2Cu_3O_7$ phase. Tc increased with increasing Ca content, x. A superconducting transition temperature of 90K was achieved for a sample with x=0.1. Thermogravimetoric data revealed that the sample with x=0.1, as well as that with x=0.0, had a high thermal stability up to a high temperature of around 850°C. These results indicate that the $(Y,Ca)Ba_2Cu_4O_8$ with Tc of 90K will have a greater potential for applications than does $YBa_2Cu_3O_7$. In addition, we will also discuss the critical current density of 90K superconductor $(Y,Ca)Ba_2Cu_4O_8$.

PHOTOELECTRON SPECTROSCOPIC STUDY OF $(Y_{1-x}Ca_x)Ba_2Cu_4O_8$

R.ITTI, T.MIYATAKE, K.IKEDA, S.TAJIMA AND N.KOSHIZUKA

Superconductivity Research Laboratory,
International Superconductivity Technology Center,Tokyo 135,
Japan

Photoelectron spectroscopic studies of polycrystalline, $(Y_{1-x}Ca_x)Ba_2Cu_4O_8$ (x=0.0-0.1) were performed. $YBa_2Cu_4O_8$ is a 80K superconducting material and substitution of Ca for Y up to 10 % raises Tc of this system towards 90K. Compared with $YBa_2Cu_3O_7$, $YBa_2Cu_4O_8$ shows an excellent thermal stability in oxygen content up to high temperature in air, and thus may be considered to be more promising for some applications than $YBa_2Cu_3O_7$. The oxygen degradation of the surface of $YBa_2Cu_3O_7$ in vacuum is well-known. It is important to investigate if the surface of $(Y_{1-x}Ca_x)Ba_2Cu_4O_8$ is stable or not in ultra high vacuum. In photoelectron spectra, we observed a clear edge at Fermi level even at room temperature. This suggests that the surface of $YBa_2Cu_4O_8$ is not degradated in vacuum and Fermi-like edge exists. Since this kind of edges were also observed by several groups for Bi-Sr-Ca-Cu-O superconductors and for $YBa_2Cu_3O_7$ (at low temperature), the existence of Fermi-like edge in normal state of high Tc superconducting materials seems to be essential for theoretical considerations.

HIGH-RESOLUTION TRANSMISSION ELECTRON MICROSCOPY OF $Y_{1-x}Ca_xBa_2Cu_4O_8$ AND ITS DEFECTS

KOJI YAMAGUCHI, TAKAYUKI MIYATAKE, TSUTOMU TAKATA, SATOSHI GOTOH and NAOKI KOSHIZUKA

SUPERCONDUCTIVITY RESEARCH LABORATORY, ISTEC, Tokyo 135, Japan

Microscopic structures of the $Y_{1-x}Ca_xBa_2Cu_4O_8$ were examined by high-resolution transmission electron microscopy. High quality single phase samples were synthesized by solid state reaction with oxygen-HIP treatments. Substitution of Ca for Y resulted in an enhancement of Tc up to 90K. Planar defects were observed in the electron micrograph. The defects appeared as white spot lines in the micrograph taken with an incident beam along the a-axis. It was deduced from the micrograph that the defects were formed by extraction of one Cu-O chain from the original $Y_{1-x}Ca_xBa_2Cu_4O_8$ structure. It turned out that the local structure near the planar defects was almost the same as that of $YBa_2Cu_3O_7$ or $YBa_2Cu_{3.5}O_{8.5}$.

(Tl, Bi, Pb)$Sr_2Ca_2Cu_3O_z$ SUPERCONDUCTORS WITH T_c ABOVE 120 K

T. Wada, T. Kaneko, H. Yamauchi and S. Tanaka

Superconductivity Research Laboratory,
International Superconductivity Technology Center,
10-13 Shinonome 1-Chome, Koto-ku, Tokyo 135 Japan

We have synthesized superconducting (Tl, Bi, Pb)$_1Sr_2Ca_2Cu_3O_z$ (1223 phase) with T_c at 122 K. The samples were prepared by the reaction between precalcined Bi-Pb-Sr-Ca-Cu-O and Tl_2O_3 powders. The x-ray diffraction pattern of the resultant oxide was successfuly indexed for a tetragonal unit cell with the lattice parameters of a = 3.82 Å and c = 15.3 Å. This compound had single (Tl, Bi, Pb) layer and triple CuO layers between the (Tl, Bi, Pb) layers. The samples showed metallic temperature dependence of resistivity and a sharp superconducting transition with zero resistance temperature, $T_c^{R=0}$, at 118 K. This zero resistance temperature was higher than a previously reported value of 115 K for a 1223 phase, $(Tl_{0.5}Pb_{0.5})Sr_2Ca_2Cu_3O_z$. Our samples also showed a sharp superconducting transition in dc magnetic susceptibility. The magnetic superconducting transition temperature, T_c^{mag}, was 122 K, which was comparable with T_c^{mag} of 122 K for $(Tl_{0.5}Pb_{0.5})Sr_2Ca_2Cu_3O_z$. The Meissner signal at 100 K of this sample was about 30 % of the perfect diamagnet.

SYNTHESIS AND CRYSTAL STRUCTURE OF A NEW FAMILY OF SUPERCONDUCTOR (Tl,Pb)(R,Sr)$_2$CuO$_5$(R=La,Nd)

Toshio NAGASHIMA, Masaya WATAHIKI, Yuh FUKAI,

Takashi MOCHIKU[A] and Hajime ASANO[A]

Fac. of Sci. & Eng., Chuo University, Bunkyo-ku, Tokyo 112, Japan

[A] Ins. of Mat. Sci., University of Tsukuba, Tsukuba, Ibaraki 305, Japan

We discovered a new family of superconductor (Tl,Pb)(R,Sr)$_2$CuO$_5$ (R=La,Nd) with transition temperature of about 40K. Starting materials of nominal composition $Tl_{1-x}LaSrCu_{1+x}O_5$ and $Tl_{0.7}LaSrCuO_5$ were mixed and pressed into pellets of 25mm in diameter 1-2mm in thickness. The samples were calcined and sintered in a covered alumina crucible at 880-900°C for 5h in air.

The crystal structure of a $TlLaSrCuO_5$ superconductor with Tc=37K was refined by Rietveld analysis of X-ray powder diffraction data.The structure of this material is tetragonal with lattice parameters a=3.772 Å,c=8.831 Å, and the space group P4/mmm.The result indicates Cu-substitution for the Tl site and/or deficiency in the Tl site, and location of La and Sr on the Sr site in the Tl-O monolayer $TlSr_2CuO_5$ compound.

The relations between Tc and x, Tc and the lattice parameter c of $Tl_{1-x}LaSrCu_{1+x}O_5$(x=0, 0.2, 0.4, 0.6) were also investigated by Rietveld analysis. Chemical composition of the samples was examined by EPMA. From these investigations, the Tc's were optimised at x=0.2, and the correlations between Tc and the lattice parameter c were also observed in this system.

SUPERCONDUCTIVITY IN THE $Bi_2(Ln,Ln*)_{3-x}Ca_xCu_2O_y$ (Ln,Ln*=LANTHANIDE AND Y) SYSTEMS

T.Ikemachi, T.Kawano, F.Munakata, A.Nozaki and H.Yamauchi

Superconductivity Research Laboratory,
International Superconductivity Technology Center,
10-13,Shinonome 1-chome,Koto-ku,Tokyo 135 Japan

New superconductors, $Bi_2Nd_{3-x}Ca_xCu_2O_y$ and $Bi_2Pr_{3-x}Ca_xCu_2O_y$ which do not contain Sr, have been successfully synthesized. The powder X-ray diffraction measurements showed that they are of either single phase or nearly single phase with the "2212" structure. Tc(onset) and Tc(endpoint) for the samples sintered in air were 47K and 24K, respectively, and those for the samples sintered in O_2 gas flow were increased by about 10K. It was likely that the increase in the hole concentration due to the introduction of oxygen enhanced the Tc. It was also discovered that, although $Bi_2Sm_{3-x}Ca_xCu_2O_y$ were nonsuperconductors, partial substitution of La for Sm resulted in superconductors with higher Tc's, e.g. $Bi_2La_{0.25}Sm_{0.25}Ca_{2.5}Cu_2O_y$ with Tc(onset) of 60K and Tc(endpoint) of 34K.

SUPERCONDUCTIVITY IN Pb-BASED COPPER OXIDES WITH 1212 STRUCTURE

T. Maeda, K. Sakuyama, S. Koriyama and H. Yamauchi

Superconductivity Research Laboratory
International Superconductivity Technology Center
10-13 Shinonome 1-Chome, Koto-ku, Tokyo 135, Japan

Pb-based 1212 superconducting copper oxides have been prepared by a solid state reaction using PbO, Sr_2CuO_3, CaO, Y_2O_3 and CuO. Sintering was performed at 900 - 1050° C for 10 - 100 h in either an oxidizing or a reducing atmosphere. Sintering in oxygen gas flow resulted in samples mainly consisting of a 1212 phase of the $(Pb_{0.5}Sr_{0.5})Sr_2(Ca,Y)Cu_2O_z$ type reported by Rouillon et al., while sintering in nitrogen gas flow yielded samples consisting of a phase of the $Pb_2Sr_2(Ca,Y)Cu_3O_z$ type which had been discovered by Cava et al.. The samples with x = 0.1 and y = 0.3 in the nominal starting composition of $Pb(Sr_{1-x-y}Ca_xY_y)_3Cu_2O_z$ sintered at 1000° C for 10 h in oxygen flow were almost of single phase 1212 containing a small amount of SrY_2O_4. These samples did not show superconductivity transition down to 4.2 K in both electrical resistivity and ac magnetic susceptibility measurements. For x = y = 1/6, the samples sintered in the same way showed superconductivity with onset temperature at 27 K and zero resistivity at 16 K. The samples were of multi-phase, including a 1212 phase as the major phase.

OXYGEN VACANCIES AND ATOMIC DISPLACEMENTS IN $(Ba_{0.85}Nd_{0.15})_2NdCu_3O_{6+z}$ AND $(Ba_{1-x}Nd_x)_2(Nd_{1-y}Ce_y)_2Cu_3O_{8+z}$

F. Izumi (National Institute for Researches in Inorganic Materials, Tsukuba), T. Mochiku, H. Akinaga, H. Asano, K. Takita (Tsukuba University, Tsukuba), H. Kito, H. Sawa, J. Akimitsu (Aoyama-Gakuin University, Tokyo), Y. Takeda (Mie University, Tsu) and M. Takano (Kyoto University, Uji)

Both $(Ba_{0.85}Nd_{0.15})_2NdCu_3O_{6+z}$ (BNCO) and $(Ba_{1-x}Nd_x)_2(Nd_{1-y}Ce_y)_2Cu_3O_{8+z}$ (BNCCO) have units that consist of $(CuO_\delta)(MO)(CuO_2)$ sheets (M: $Ba_{1-x}Nd_x$). The crystal structures of as-grown and fully oxidized samples of BNCO and BNCCO were refined by Rietveld analysis of TOF neutron diffraction data. They are tetragonal, and, therefore, oxide ions which partially occupy positions between two MO sheets are disordered on ab planes. The occupation probabilities of these oxygen sites affect their superconducting properties in striking manners. The Cu and O atoms on the CuO_δ sheets and the O atom on the BaO sheets are evidently displaced from ideal positions, which must be due to the substitution of small Nd^{3+} ions for large Ba^{2+} ions.

RIETVELD STRUCTURE REFINEMENT OF SUPERCONDUCTING $YBaSrCu_3O_{7-\delta}$ USING X-RAY AND NEUTRON POWDER DIFFRACTION DATA

E. Akiba, H. Hayakawa, M. Mizuno, F. Izumi# and H. Asano*
National Chemical Laboratory for Industry, 1-1 Higashi, Tsukuba, Ibaraki 305 Japan
#National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaraki 305 Japan
*Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305 Japan

The structure and superconductivity of high-Tc oxide superconductors of $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ were investigated by Rietveld structural analysis and by measurement of electric conductivity. At the composition of $YBaSrCu_3O_{7-\delta}$, it was found that the Tc rose discontinuously with the amount of Sr substitution. Then, the structure of $YBaSrCu_3O_{7-\delta}$ was refined precisely using X-ray and time-of-flight neutron powder diffraction data. The structure of the high-Tc phase of $YBa_2Cu_3O_{7-\delta}$ and related compounds has been refined by Rietveld analysis using a orthorhombic model but it has been noticed that some calculated peaks of the diffraction pattern did not fit to the observed ones. It is well known that the high-Tc phase has the micro twin plane of (110). Therefore, we adopted a new structural model for Rietveld analysis which contains a usual orthorhombic phase and a tetragonal phase representing the structure around the micro twin plane. The fitness of refinement using the new model was better than the orthorhombic model. It is clear that a contribution of the microtwin should be taken into consideration to refine the structure of $YBa_2Cu_3O_{7-\delta}$ and related compounds.

EFFECT OF OXYGEN HIP ON SUPERCONDUCTING PROPERTY OF HIGH-Tc OXIDE SUPERCONDUCTORS

Kazuyuki SHIBUTANI, Seiji HAYASHI, Yoshito FUKUMOTO, Rikuo OGAWA and Yoshio KAWATE

Superconducting and Cryogenic Technology Center, Technology Development Group, Kobe Steel,Ltd.,1-5-5,Takatsukadai,Nishi-Ku, Kobe 673-02, Japan

Oxygen Hot Isostatic Pressing (O_2-HIP) is effective for creation of new phases which are stabilized under high pressure and decreasing of oxygen deficiency.

$RBa_2Cu_3O_x$ (R=Y,Ho...) system and $La(Sm_{1-x}Sr_x)CuO_4$ system with T*-phase structure were studied. The effect of O_2-HIP on both systems was studied through the measurements of the magnetic susceptibility by using SQUID magnetometer and measurements of X-ray diffraction patterns for identification of the contained crystalline phases. The dependence of O_2-HIP treating conditions (Pressure and Temperature) on the phase creation and superconducting property was studied on $RBa_2Cu_3O_x$ system. In result, the second stabilized phase with longer c-axis than $RBa_2Cu_3O_x$ was obtained after O2-HIP treatment. The dependence of Sr-concentration on the amount of Meissner signal and transition temperature was studied on $Sm(La_{1-x}Sr_x)CuO_4$ system with T*-phase structure. In result, there was the maximum value of Meissner signal at x=0.25, and the dependence of Sr-concentration on Tc was small.

DETERMINATION OF OXYGEN CONTENT OF $YBa_2Cu_3O_{7-y}$ SUPERCONDUCTOR

YOKO SUYAMA, MAMORU MATSUMOTO, AND TOSHITAKA HAYAKAWA
Japan Fine Ceramics Center, Nagoya, Japan

The superconductive properties of $YBa_2Cu_3O_{7-y}$ are strongly dependent on the chemical composition, particularly the oxygen content. Therefore, the accurate determination of the oxygen content along with the other constituent elements is important fundamentally to elucidate the mechanism and properties of superconductive materials.

In this study, an analytical method to determine the oxygen content accurately was examined by using an oxygen analyzer. The oxygen content was able to determine by 4 orders of magnitude as molar ratio, with a standard deviation of 0.07, under the controlled analytical conditions.

The lattice constants of $YBa_2Cu_3O_{7-y}$ change with the oxygen content. the relationship between the lattice constants and the oxygen content was discussed.

FERROELASTICITY IN SUPERCONDUCTING $YBa_2Cu_3O_y$ AND La_2CuO_4 SINGLE CRYSTALS

A. SAWADA,[a] Y. NISHIHATA,[a] T. HATANAKA,[b] K. OKA,[c] and H. UNOKI[c]

a) Department of Physics, Okayama University, Okayama 700, JAPAN
b) Synthetic Crystal Research Laboratory, Nagoya University, Nagoya 464-01, JAPAN
c) Electrotechnical Laboratory, Tsukuba 305, JAPAN

It is known that $YBa_2Cu_3O_y$ (YBCO) and La_2CuO_4 (LCO) crystals undergo tetragonal-orthorhombic phase transitions at 600°C and 200°C, respectively, and that both crystals have domain structures at room temperature.

Using a polarizing microscope we have found that domain walls in YBCO can move on applying external compressive stress along [100] axis in the tetragonal axes at sample temperature of about 200°C to 350°C. The coercive stress is about 1000kgw/cm^2 at 200°C. Single domain samples with C plane of about 400x150μm^2 were obtained by ferroelastic domain switching from multi-domain ones.

Domain structures in La_2CuO_4 crystals have been observed for the first time on both as-grown surfaces and freshly-cleaved surfaces. Usually a number of parallel domains with the width of about 1μm to 10μm are densely lined up. Domain walls are found to be parallel to {100} planes in the tetragonal axes using x-ray diffraction. Domain walls in LCO crystals have been found to move at room temperature upon application of external compressive stress.

Thus both YBCO and LCO crystals can be called ferroelastic ones. Single-domain crystals obtained by ferroelastic domain switching will be useful for studying anisotropic properties of, for example, electrical conductivity and infrared spectra. Furthermore, ferroelastic technique which can change the density of domain walls will be useful for studying superconducting properties such as the relation of critical current to the density of domain-walls which may work as pinning centers of magnetic flux.

PSEUDO-ELASTIC DEFORMATION AND ENVIRONMENT-INDUCED STRUCTURAL CHANGES IN OXIDE SUPERCONDUCTORS

Nobutaka Narita, Kenji Higashida and Shotaro Mishina

Department of Metallurgy, Kyoto University
Yoshida-honmachi, Sakyo-ku, Kyoto 606, Japan

Pseudo-elastic behavior and environment-induced structural changes were investigated using $YBa_2Cu_3O_Y$(YBCO) and $Bi_{0.7}Pb_{0.3}SrCaCu_{1.8}O_Y$(BPSCCO) ceramics with particular attention to the role of oxygen vacancies. The YBCO becomes capable of pseudo-elastic deformation with increasing temperature as long as the temperature lies within the range where orthorhombic phases are stable. X-ray diffraction analyses found the occurrence of pseudo-elastic deformation by deformation twinning in the YBCO. The deformation twinning is accomplished by the reorientation of oxygen-vacancy arrays accompanying the mutual conversion of a and b axes in the orthorhombic phase. Oxygen vacancies are sufficiently mobile at elevated temperatures because the rapid increase of oxygen-vacancy content is observed during aging in vacuum. The presence of excess oxygen vacancies promotes environment-induced structural changes through the enhanced occlusion of some environmental elements such as H atoms. When the excess vacancy content is reduced by doping Mn^{4+} or F^- ions, the structural changes can be retarded in the YBCO. On one hand, the BPSCCO shows relatively large resistance to the structural changes. However, the BPSCCO once fired in a low Po_2 (oxygen partial pressure) atmosphere in order to obtain single high Tc phase suffers severe structural changes in water vapor. Firing in a low Po_2 atmosphere causes the mass decrease of a specimen, indicating the increase of oxygen-vacancy content. It is thus evident that the structural changes as well as the deformation twinning are mainly controled by the mobility and activity of oxygen vacancies in oxide superconductors.

MICROSTRUCTURAL CHARACTERIZATION OF $YBa_2Cu_3O_{7-x}$ PREPARED BY THE QUENCH AND MELT GROWTH (QMG) PROCESS

Akihiko Hayashi, Masao Kimura, Mitsuru Morita, Keiichi Kimura, Kenji Doi, Katsuyoshi Miyamoto, Kiyoshi Sawano, Munetsugu Matsuo and Shoichi Matsuda

R & D Laboratories-I, Nippon Steel Corporation, Kawasaki 211, JAPAN

The YBCO bulk material prepared by the Quench and Melt Growth (QMG) process was characterized from the microstructural and crystallographic point of view. The microstructure of the material was studied using a polarized optical microscope. The crystal texture was investigated as follows. X-ray diffraction intensity was measured and analyzed at a Bragg angle by tilting the specimen relative to the incident X-ray beam.

The microscopic observation showed that the material was a composite of $YBa_2Cu_3O_{7-x}$ (123) matrix and Y_2BaCuO_x (211) dispersoid with striations and cracks. X-ray diffraction study indicates that the material consists of some grains (several mm in size), each of which contains a few domains arranged within a range of several degrees.

In conclusion, the QMG-processed material is found to be a 211 phase-dispersed large 123 crystal.

HOT DEFORMATION AND SUPERCONDUCTIVITY OF $YBa_2Cu_3O_{7-x}$ CERAMICS

Yasuharu Kodama and Fumihiro Wakai

Government Industrial Research Institute, Nagoya,
1-1, Hirate-cho, Kita-ku, Nagoya, Japan

Compressive deformation of $YBa_2Cu_3O_{7-x}$ at elevated temperature (850°C~960°C) was investigated, and its influence on superconductivity was also studied.

The dense (density, 5.8~6.0 g/cm^3) and the porous (density, 4.5 g/cm^3) materials were used for the compression test. The compression tests were performed under 'constant cross-head speed' condition. The dense materials deformed at constant flow stress after the yield point, while the flow stress of porous materials gradually increased with strain. The former behavior was caused mainly by plastic deformation, and the latter mainly by densification.

The resistivity of the inside of dense materials after the compression was high, and indicated that there was little superconducting phase. On the other hand, the inside of the porous materials indicated superconductivity ($T_{c\ on}$ = 88K), although most of the part behaved as semiconductor. The reason is that the cooling rate after compression test was too quick to induce phase transition from tetragonal to orthorhombic, and that a little oxygen could diffuse through pores in porous materials.

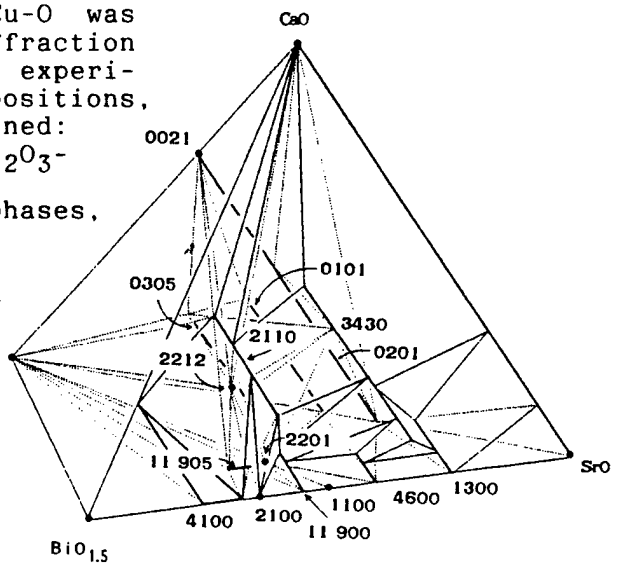
The effect on superconductivity caused by lattice distortion and/or by densification will also be discussed.

PHASE EQUILIBRIA IN Bi_2O_3-SrO-CaO-CuO SYSTEM AT 1123K IN AIR

R.O.Suzuki, S.Kambara, H.Tsuchida, K.Shimizu and K.Ono

Department of Metallurgy, Kyoto University, Yoshida-Honmachi, Sakyo-ku, Kyoto 606 JAPAN.

Phase equilibria in Bi-Sr-Ca-Cu-O was investigated mainly by X-ray diffraction measurements. Summarizing the experimental results at about 200 compositions, the following results were obtained:
1) The ternary equilibria in Bi_2O_3-SrO-CaO, Bi_2O_3-SrO-CuO and SrO-CaO-CuO were clarified and new phases, [0178] (Bi=0,Sr=1,Ca=7,Cu=8,O=?) and [2110], were found.
2) 7 quaternary phase equilibria and 5 ternary equilibria were confirmed inside the tetrahedra of Bi_2O_3-SrO-CaO-CuO.
3) No diffraction for "High Tc phase" [2223] was detected in these conditions, but "Low Tc phase" [2212] was at least in equilibrium with CaO, CuO and 4 solid solutions ([3430], [0305], [0021]-[0201] and [2201]).



SUPERCONDUCTIVITY IN $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_y$

Tae-Su Han, Akihito Sawa, Hiromoto Uwe, Tunetaro Sakudo
Institute of Applied Physics, University of Tsukuba,
Tukuba, Ibaraki 305, Japan

Effect of the Ce-ions substitution for the Ca ions in $Bi_2Sr_2CaCu_2O_y$ with the superconducting transition temperature of Tc=80K has been investigated. Up to the Ce concentration x=0.5, the powder x-ray diffraction exhibits a pattern similar to the non-substituted one with the decreasing c-axis and increasing a-axis. The resistivity measurement shows that Tc slightly increases first with the substitution and then tends to decrease above x=0.05. Further, the system undergoes the metal insulator transition between x=0.25 and 0.3. The Hall coefficients stay positive and increases with substitution. The overall behaviors quite resemble to those observerd for $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$, provided that $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_y$ should correspond to $Bi_2Sr_2Ca_{1-2x}Y_{2x}Cu_2O_y$ on account of the difference of the formal valences of Ce and Y. The phase diagram of the superconductive and antiferromagnetic phases as a function of the substitution will be discussed on the comparison with those of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$, $YBa_2Cu_3O_y$, and $La_{2-x}Sr_xCuO_4$.

PREPARATIVE AND STRUCTURAL STUDIES ON VARIOUS SUBSTITUTIONS IN THE Bi-Sr-Ca-Cu-O SYSTEM

Zhu Wenjie Chen Fengxiang Li Neng Li Hongyu
Lin Bingxiong Tang Youqi
Institute of Physical Chemistry , Peking University
Beijing, P.R. China

The samples with the norminal compositions of $Bi_{2-x}M_xSr_2Ca_2Cu_3O_y$ (M= Pb, In, Sb, Nb) and $Bi_{2-x}Pb_{x+y}M_xSr_2Ca_2Cu_3O_y$ (M= In, Sb, Nb) were prepared and investigated. X-ray diffraction patterns reveal that only the statistical substitution of lead for bismuth results in the formation of the 110K phase. With the introduction of lead, indium, antimony, and niobium get into bismuth positions but with a little amount, among which indium makes some improvement on properties. In the crystal structure of a rather homogeneous phase $Bi_{1.7}Pb_{0.2}In_{0.1}Sr_2Ca_2Cu_3O_y$ determined by using Rietveld profile analysis, adjacent layers with one oxygen layer in between display a perfact Aurivillius type structure, rather than the rocksalt type structure observed in 2212 phase by Tarascon et al. The substitutions of lead, which could be accommodated in a square pyramid, and indium lead bismuth and oxygen layers to stack regularly. As a result, extra $Ca(CuO_2)$ slabs incorporate into 2212 phase without distortion, forming 2223 high Tc phase, and the structural unit $(O_2Cu)Ca(CuO_2)Ca(CuO_2)$ shifts to tetragonality, which were suggested to be the origin of the Tc raise of about 20K and narrow transition width.

EFFECT OF ELEMENTAL SUBSTITUTION ON THE SUPERCONDUCTIVE PROPERTIES IN $Bi_2Sr_2Ca_{n-1}Cu_nO_y$

Shiro KAMBE, Teruyuki MATSUOKA[+], Maki KAWAI[++],
Tomoji KAWAI[+++] and Makoto Takahashi[+]

F.R.P., The Institute of Physical and Chemical Research, 2-1, Hirosawa, Wako, Saitama 351-01, Japan

[+] International Christian University, 3-10-2, Osawa, Mitaka, Tokyo 181, Japan

[++] Research Laboratory of Engineering Materials, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

[+++] The Institute of Industrial and Scientific Research, Osaka University, Mihogaoka, Ibaraki, Osaka 567, Japan

Effect of elemental substitution on the physical properties in $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ has been studied. It has already been revealed that the addition of Pb to Bi-Sr-Ca-Cu-O superconductors enhances n=3 phase formation. It is interesting to know whether Pb^{2+} substituted for Bi^{3+} can be one of the hole donors in this system. We have found that Pb is substituted for Bi homogeneously in both n=2 and 3 phases and that the hole concentration of the system can be controlled by the substitution. In the case of n=2 phase, $Bi_{2-2x}Pb_{2x}Sr_2Ca_{n-1}Cu_nO_y$ of x=0.3 decreased Tc from 80K to 75K. The decrease of Tc can be explained by the fact that the hole concentration of the system is controlled by the amount of Pb substitution and that the value of $\triangle Tc/\triangle hole$ in the observed region is negative, which means that hole is overdoped in the region. In the case of n=3 phase, the change of Tc was found to be much smaller than that in n=2 phase. This indicates that the observed $\triangle Tc/\triangle hole$ in n=3 phase is nearly zero where that of n=2 phase in the same region of the hole concentration is negative. Substitution effects in other elements such as sulfur will also be reported.

THE FORMATION AND STABILITY OF SUPERCONDUCTING PHASES IN Bi-Sr-Ca-Cu-O SYSTEM

Shigeki KOBAYASHI and Shigetaka WADA

Toyota Central Research and Development Labs., Inc.
Nagakute, Aichi 480-11, JAPAN

The effects of sintering conditions and Pb addition on the formation of superconducting phases have been studied. The optimum sintering temperature range was very narrow. The formation of high Tc phase was enhanced by preheating at the temperature range of partial melting. Sintering under the atmosphere of low oxygen pressure was effective to form high Tc phase for Pb added specimens, but deteriorated the weak links and reduced the shielding effect significantly.

The stability of superconducting phases during low temperature annealing was also examined. Annealing did not affect the amount of superconducting phases. The transition temperatures changed but in a different way for the low Tc and high Tc phases. These results clearly indicate that oxygen evolution takes places during annealing and affects the properties as observed in Y-Ba-Cu-O system.

GROWTH OF HIGH-T_c PHASE and PARTIAL MELTING IN Pb-DOPED Bi-Sr-Ca-Cu-O

Kentaro OHBA, Akira ISHIDA, Kiyotoshi IWASAKI, Hideaki KUWAJIMA,
Hideki NOJI*, Akihiro KIRIHIGASHI* and Akio OOTA*

Technical Research and Development Laboratories,
Topy Industries Ltd., Akemi-cho, Toyohashi-shi, Aichi 440
*Department of Electrical and Electronic Engineering,
Toyohashi University of Technology, Toyohashi-shi, Aichi 440

The role of partial melting in the growth process of the high-T_c phase was studied on Pb-doped Bi-Sr-Ca-Cu-O through XRD, DTA, EPMA, resistivity and susceptibility measurements. The samples with nominal composition $Bi_2Pb_{0.6}Sr_2Ca_2Cu_3O_x$ were prepared by sintering at T_s=835∿855°C for 5∿160h in air, after the calcination at 800°C for 12h in air.

The DTA study showed that the partial melting starts to occur at T_{pm} ≈842°C upon heating. The XRD and SEM images showed that the partial melting enhances the growth rate of the high-T_c phase and yields a nearly-single phase within 40h, while it takes much more time without partial melting. The EPMA study revealed that the Pb in high-temperature sintering at $T_s > T_{pm}$ dissipates faster than the one in low-temperature sintering at $T_s < T_{pm}$. This is related to the behavior of melting point T_m from DTA that the T_m is significantly raised by the partial melting.

The superconducting transition temperature $T_c(\rho=0)$ from resistivity measurements shows a notable difference from XRD result. The maximum value of $T_c(\rho=0)$ of about 105K can be achieved only when the high-T_c phase develops gradually in the prolonged sintering at temperature just below T_{pm} without partial melting. The high-temperature sintering at $T_s > T_{pm}$ causes a lowering of $T_c(\rho=0)$, while it promotes a rapid growth of the high-T_c phase due to the participation of the partially melted phase. The lowering of $T_c(\rho=0)$ seems to be attributed to the disturbance in current paths at the grain boundaries.

FORMATION OF A HIGH Tc PHASE IN Pb-Bi-Sr-Ca-Cu-O SUPERCONDUCTOR

Shunichi Nishikida

Sumitomo Metal Ind. Ltd.
16 Sunayama, Hasaki, Ibaraki 314-02

The formation of a high Tc phase (2223) in Pb-Bi-Sr-Ca-Cu-O superconductor was observed by means of interface reaction between low Tc phase (2212) and Pb-Sr-Ca-Cu-O mixed oxides.

By X-ray diffraction and electron-probe micro-analysis, it was shown that there were 2212, $(Ca,Sr)_2PbO_4$, $(Ca,Sr)_2CuO_3$, CuO and other unidentified minor phases in calcined powders or samples sintered at as low temperature as not to form 2223. Bi atoms were included only in 2212 but, other atoms were in both 2212 and residual oxides. The residual oxides, from which Bi was excluded, were pressed on the surface of 2212 green body. This layered samples was sintered at 840°C in air. At the interface of 2212 and residual oxides, consisting of $(Ca,Sr)_2PbO_4$, $(Ca,Sr)_2CuO_3$ and CuO, 2223 crystals grew like needles. However, 2223 crystals did not utterly cover the interface. This means that in this reaction, the nucleation of 2223 occurs very slowly. The growth of 2223 crystals were directed into both 2212 layer and the residual oxides. This suggests that the crystal growth of 2223 is strongly controlled by the diffusion of Bi atoms for the growth in the residual oxides and Ca and Cu atoms for that in 2212 through the 2223 crystal formed or the interface between 2223 and the matrix.

When the individual oxides such as $(Ca,Sr)_2PbO_4$, $(Ca,Sr)_2CuO_3$ or CuO separately or combination of $(Ca,Sr)_2CuO_3$ and CuO were used as reactants with 2212, the formotion of 2223 was not observed.

THE FORMATION PROCESS OF THE HIGH-T_c PHASE IN THE Bi-Pb-Sr-Ca-Cu-O SYSTEM

Hiroyuki ITO, Yasunori IKEDA, Shinichi SHIMOMURA, Zenji HIROI, Mikio TAKANO, Jun TAKADA*, Kiichi ODA* and Yoshichika BANDO

Institute for Chemical Research, Kyoto Univ. Uji, Kyoto-fu 611 Japan
*Faculty of Engineering, Okayama Univ., Okayama 700 Japan

The formation process of the 2223 (high-T_c) phase in the Bi-Pb-Sr-Ca-Cu-O system has been studied for a starting composition Bi:Pb:Sr:Ca:Cu=0.9:0.2:1:1:1.6 by changing firing temperature from 780°C to 860°C in air.

Phase identification was carried out by means of XRD, SEM, TEM and also by measurements of DC magnetization with a SQUID magnetometer and DC resistance. TG-DTA thermal analysis was also conducted.

The temperature of 810°C has been found to be the border above which the formation of the 2223 phase is accelerated. Below 810°C, four phases coexist in equilibrium which are the 2212 and 2201 phases, Ca_2PbO_4, and CuO. Above 810°C, the 2223 and 2212 phases and Ca_2PbO_4 coexist, and the amount of the 2223 phase is increased with increasing temperature at the expense of Ca_2PbO_4 and the 2212 phase. CuO and the 2201 phase were not detected by XRD above 810°C. Thermal analysis was carried out for various combinations of the phases appearing below 810°C. As a result a certain combination of the 2201 phase, Ca_2PbO_4, and CuO showed an endothermic peak at around 810°C. This has been attributed to the occurrence of a liquid phase.

From the present experiments, we conclude that the liquid phase accelerating the formation of the 2223 phase is formed from the 2201 phase, CuO, and Ca_2PbO_4. The high-T_c phase should be formed from the reaction of the 2212 phase with the liquid phase.

PREPARATION OF HIGH T_C PHASE IN Bi-Sr-Ca-Cu-O SYSTEM BY MEANS OF ADDITION OF Ca_2PbO_4

Hajime ITO, Masaaki MATSUI and Masao DOYAMA, Department of Materials Science and Engineering, Faculty of Engineering, Nagoya University, Nagoya 464-01, Japan

In a new superconducting Bi-Sr-Ca-Cu-O system discovered by Maeda et al., two main superconducting phases called as 2223(T_C=110K) and 2212(T_C=80K) are formed. The low T_C phase was easily obtained by the sintering method, while it was considerably difficult to refine the single high T_C phase. Great deal of efforts were paid to purify the 2223 phase and then Takano et al. reported that doping of Pb was extremely effective.

In the present report, we propose another method to prepare the single high T_C phase by means of mixing and sintering Ca_2PbO_4, CuO and the sample of 2212. The mixture of 2212 : Ca_2PbO_4 : CuO = 1 : 0.4 : 1 was pressed into pellets and sintered at 1123K for 6 days. According to the powder X-ray diffraction patterns, the sintered bulk sample was almost single high T_C phase and the T_C^{on} and T_C^{off} observed by the resistivity measurement were 115K and 106K respectively.

The high T_C phase has a structure inserted by two extra layers of CuO and CaO into a 2212 structure. If Ca_2PbO_4 and CuO which are stable at high temperatures supplies CaO and CuO, high T_C phase is expected to be formed. This process might be applied to the preparation of thin films of the single high T_C phase.

INCREASED CRITICAL TEMPERATURE IN Bi-Sr-Ca-Cu-O OXIDE SYSTEM

Kumiko Imai and Hironori Matsuba
Yokohama R&D Laboratories The Furukawa Electric Co.,Ltd.
2-4-3,Okano,Nishi-ku,Yokohama,Japan-220

The various superconducting phase in the Bi-Sr-Ca-Cu-O oxide system have been reported. Much research has been conducted to obtain high critical temperature,Tc, single phase with a transition temperature of 110K, of which the nominal composition is $Bi_2Sr_2Ca_2Cu_3O_{10+y}$ (referred to as the 2223 phase).
It has been reported that the most of the high Tc single phase has been obtained by substituting of Pb, though more than hundreds of hours and a physical process are necessary. The low Tc $Bi_2Sr_2CaCu_2O_x$ phase (referred to as the 2212 phase) with a transition temperature of 85k can be obtained with a shorter sintering time and with a simple process compared to the high Tc phase. It has been reported that Tc of the 2212 phase is changed sensibly by the processing conditions, and the maximum 'zero' resistivity critical temperature of the 2212 phase reached 85K.

We found a method to obtain superconductors composed mostly of the 2212 phase with a higher Tc of 95K and with excellent critical current Jc, and consequently, found that the critical temperature varies with annealing conditions. In this report, the dependence of Tc on annealing conditions and the electric behaviors of these samples are described.

HRTEM OBSERVATION ON MIXED PHASES AND INTERFACES IN HIGH-Tc Bi-BASED SUPERCONDUCTORS

S.Horiuchi, K.Shoda*, S.Wu** and Y.Matsui
National Institute for Research in Inorganic Materials, Tsukuba, Ibaraki 305, Japan
*Ube Industries Ltd. Ube, Yamaguchi 755, Japan
**Institute of Physics, Chinese Academy of Science, Beijing, China

For a series of superconductors $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+x}$ (n=1~3), showing the critical temperatures Tc at about 20, 85 and 110K respectively, we have examined the mixing state of the phases, especially the microstructures at interfaces, by high-resolution transmission electron microscopy (HRTEM). A specimen prepared by quenching from the temperature, at which it has been partially melted, is consisted of major component of the (2201) phase with a minor component of the impurity phases, which are $(Ca,Sr)_3Cu_5O_y$ and Ca_2CuO_3 both with the shape of square column. When the specimen is annealed at 500°C in air, it shows an abrupt decrease in resistivity with Tc at about 75K and this is due to the formation of small amount of the (2212) phase, which increases the volume fraction on annealing at higher temperature. The (2233) phase becomes the major component on annealing at 880°C and this must be due to the phase decomposition. The results will be discussed from the viewpoint not only of Tc but also of the critical current density Jc.

MODULATED STRUCTURES IN HIGH-T_c SUPERCONDUCTING OXIDES: Bi-Sr-Ca-Y-Cu-O AND Tl-Ba-Ca-Cu-O

Y. Inoue, M. Hasegawa and M. Yamanaka
Central Engineering Laboratories, Nissan Motor Co., Ltd.,
1, Natsushima-cho, Yokosuka 237, Japan
Y. Koyama
Department of Materials Science and Engineering, Waseda University,
Ohkubo, Shinjuku-ku, Tokyo 169, Japan

Features of modulated structures in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$, $Bi_4Sr_3Ca_{3-v}Y_vCu_4O_w$ and $Tl_2Ba_2Ca_2Cu_3O_z$ have been investigated by means of electron microscopy.

(1) $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$: The period of one-dimensional modulated structure along the b axis decreases linearly from about $4.8b$ at $x = 0.0$ to $4.0b$ at $x = 0.8$, where b is a lattice parameter of the structure without the modulation. In addition to one-dimensional structure, a new structure modulated along the a and b axes is found in $0.8 < x \leq 1.0$. High-resolution electron micrographs show that the new structure is characterized by the periodic array of wavy stripes along the b axis.

(2) $Bi_4Sr_3Ca_{3-v}Y_vCu_4O_w$: The period of one-dimensional modulated structure along the b axis decreases linearly from about $4.6b$ at $v = 0.0$ to about $4.2b$ at $v = 2.0$. In electron diffraction patterns, diffuse streaks along the a axis are also observed in $v = 2.0$. Corresponding to the diffuse streaks, defects like antiphase boundary are found in high-resolution electron micrographs with $v = 2.0$.

(3) $Tl_2Ba_2Ca_2Cu_3O_z$: In addition to a diffuse scattering around a fundamental spot, thermal diffuse scattering due to a transverse phonon (e // [010]) propagating along the [100] direction was found in electron diffraction patterns of the sample with T_c of 117 K. The scattering has an intensity maximum at the middle between two fundamental spots along the <100> directions, and its intensity increases with decreasing temperature.

MODULATED STRUCTURES OF Bi-BASED HIGH-T_c SUPERCONDUCTING OXIDES

Y. Hirotsu, N. Yamamoto, O. Tomioka, K. Miyagawa, Y. Nakamura*, Y. Inoue** and S. Nagakura

Faculty of Engineering, Nagaoka University of Technology, Nagaoka, Japan *Department of Metallurgical Engineering, Tokyo Institute of Technology, Tokyo, Japan **Central Research Laboratory, Nissan Automobile Co., Ltd., Yokosuka, Japan

Since the discovery of superconducting phases in Bi-Ca-Sr-Cu-O system, extensive studies on their structures and physical properties have been made by adding other elements to these phases. The addition of Pb has been reported to stabilize the superconducting 2223 phase with T_c 110K. Y has been thought to replace Ca, although the complete replacement of Ca produces an insulating phase. These Bi-based superconducting oxides show incommensurate or commensurate modulated structures depending on the system. In this study, we have investigated structural differences of the modulated structures in the Bi-Ca-Sr-Cu-O, Bi-Ca-Y-Sr-Cu-O and Bi-Pb-Ca-Sr-Cu-O systems by means of high-resolution electron microscopy and electron diffraction. Based on both the high-resolution images and extinction rules of electron diffraction, structural models of the atomic displacive modulations are presented for the modulated structures of these oxide systems. In the modeling, atomic displacive longitudinal and transverse waves were taken into account.

Peparation of Bi(Pb, Sb)-Sr-Ca-Cu-O System Superconductors through Sol·Gel Method.

Yoshio MASUDA, Tsuyoshi TATEISHI, Kazuyuki SIBUTANI, Rikuo OGAWA and Yoshio KAWATE

Superconducting and cryogenic Technology Center, Technology Developement Group, Kobe Steel Ltd., 5-5 1-choume, Takatsukadai, nisi-ku, Kobe 673-02

We synthesized Bi(Pb,Sb)-Sr-Ca-Cu-O Superconducting oxides from acetate aqeous solutions through sol·gel method. Acetates with composition of Bi:(Pb):Sr:Ca:Cu= 0.96:(0.24):1:1.1:1.6 were dissolved in the solution of water and acetic acid, and the solution containing Sb element was prepared by adding nitric acid solution in which metal Sb was dissolved to the Bi-Sr-Ca-Cu acetic solution. After adjusting the pH of the solution by adding ammonia water, the solutions were kept at 80℃ and concentrated. Transparent gels were obtaind limitedly under the condition of pH=5.2～5.8 from the solutions containing no Sb element. In the solution containing Sb element, coloidal particles had been produced and the gels obtained from this solution were not transparent. These gels were heated at 850℃ for 12 hours in air. From the result of X-ray diffraction low-Tc phase was formed mainly in the Bi-Sr-Ca-Cu-O and Bi-Pb-Sr-Ca-Cu-O systems, but in the Bi-Sb-Sr-Ca-Cu-O system, no superconducting phases were formed. Magnetic susceptibi-lity was measured by SQUID and it was found that the specimen in the Bi-Sr-Ca-Cu-O system showed diamagnetic susceptibility below 75K and the specimen in the Bi-Pb-Sr-Ca-Cu-O system showed diamagnetic susceptibility below 108K and had a shoulder around 75K.

EFFECTS OF TOTAL HIGH PRESSURE AND HIGH OXYGEN PARTIAL PRESSURE DURING O_2-HIP SINTERING ON Bi-Sr-Ca-Cu-O SUPERCONDUCTOR

Hiroshi SEINO, Kozo ISHIZAKI and Masasuke TAKATA*

Department of Material Science and Engineering, School of Mechanical Engineering, Nagaoka University of Technology.
*Department of Electrical Engineering, Nagaoka University of Technology.
Nagaoka, Niigata 940-21, Japan.

Superconducting Bi-(Pb)-Sr-Ca-Cu-O were synthesized by a capsule-HIP and a O_2-HIP processes without any additional treatment for the first time. In the capsule-HIP sintering process, the high-T_c phase was obtained due to enhanced Ca diffusion by high pressure during HIPping. For the O_2-HIP treatment, the high pressure and the high oxygen partial pressures allowed shorter sintering time at a higher temperature than conventional methods under 0.1MPa. The effects of high pressure and a high oxygen partial pressure were (PO_2) obtained by a *HIP phase diagram* which is proposed by our laboratory, and whose were confirmed by O_2-HIP sintering. In the *HIP phase diagram* under P_{total}=100MPa, optimum temperatures for obtaining high-T_c phase are about at between 1303-1353K (PO_2: from 10MPa to 20MPa). The results of O_2-HIPping agree well with theoretical calculation.

SUPERCONDUCTIVITY OF HIGH T_c Tl-Ba-Ca-RE-Cu-O (RE=lanthanoid) SYSTEM

Satoru Nakajima*, Masae Kikuchi, Norio Kobayashi, Hideo Iwasaki, Daisuke Shindo, Yasuhiko Syono and Yoshio Muto

*Hachioji Research Center, CASIO Computer Co.,Ltd,Hachioji 192, Japan
Institute for Materials Research, Tohoku University, Katahira, Sendai 980, Japan

Bulk superconductors of the single Tl layered Tl-Ba-Ca-RE(=lanthanoid)-Cu-O system have been synthesized to investigate substitution effects of trivalent RE for Ca.
Crystal structures were studied by X-ray powder diffraction and superconducting properties were determined by resistivity and DC susceptibility measurements.
T_c of the Y substituted system, $TlBa_2Ca_{1-x}Y_xCu_2O_7$, increases with increasing Y concentration up to x=0.2-0.3, where it turns down and reaches non-superconductor at x=0.5.
The maximum T_c of the Y substituted system achieved at x=0.2-0.3 and the average Cu valence is 2.4-2.35 which is calculated from stoichiometry.
The dependence of T_c on the concentration of Y substituted for Ca suggests an over-doping state in x<0.2-0.3.
We will also report effects of substitution of other lanthanoid ions on superconductivity in terms of Cu-O bond lengths and ionic radii of substituted cations.

X-RAY ABSORPTION STUDIES OF Tl-Ba-Ca-Cu-O SUPERCONDUCTORS

Hirotaka YAMAGUCHI, Hiroyuki OYANAGI, Hideo IHARA,
Ryoji SUGISE* and Takehiko SHIMOMURA**
Electrotechnical Laboratory, Umezono, Tsukuba, Ibaraki 305
**Ube Industries Ltd., Ube, Yamaguchi 755*
***Unitika R&D Center, Uji, Kyoto 611*

The local structures and valence states of $Tl_1Ba_2Ca_{n-1}Cu_nO_{2n+3}$ (Tl_1-system) and the $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ (Tl_2-system) have been investigated by extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) on the Cu K-edge.

XANES spectra show apparent differences between the Tl_1- and the Tl_2-systems, which shows the valence of copper in the Tl_2-system is higher than that in the Tl_1-system. Since the difference of valence might be due to that of oxygen-vacancy and the Tl_2-system exhibits higher T_c than the Tl_1-system, it is found that oxygen-vacancy plays important roles of the superconductivity.

In the Fourier transforms of EXAFS, the peak corresponding to apical oxygens of CuO_5 pyramids is hardly found. This means the apical oxygens are highly disordered or fluctuated. The Cu-O vibrational properties are also studied by the temperature dependence of the EXAFS.

STRUCTURE AND SUPERCONDUCTIVITY OF $Tl_2Ca_3Ba_2Cu_4O_x$ SINGLE CRYSTALS

T. Kotani, T. Nishikawa, H. Takei and K. Tada
Basic High-Technology Laboratories, Sumitomo Electric Industries, LTD
1-3, Shimaya 1-chome, Konohanaku, Osaka, 554, Japan

Crystal structure and superconducting properties of $Tl_2Ca_3Ba_2Cu_4O_x$ single crystals were investigated. Firstly, we estimated the phase diagram of the $Tl_2Ca_{n-1}Ba_2Cu_nO_x$ system. Based on this phase diagram, 2324-phase single crystals with typical dimensions of from 0.25 to 1mm^2 were grown by the flux method. The superconducting onset transition temperatures of grown crystals, determined by DC SQUID magnetometer, were 113 to 115K. According to an X-ray diffraction measurement, the lattice constant of the c-axis was 42.0Å, and the crystal was confirmed to be single phase of 2324. Moreover, we applied high-resolution transmission electron microscopy(TEM) for precise structural analysis of 2324-phase in the Tl system. The stacking structure having four Cu-O layers separated by double Tl-O layers can be directly seen from these observations. The periodic spacing of the stacking was consistent with a value measured by means of X-ray diffraction. However, some singular stacking structures with different numbers of Cu-O and Tl-O layers were observed between the normal stacking layers. Detailed results of the TEM observations for 2324-phase single crystals will be reported.

SUPERCONDUCTIVITY OF THE Tl-Ba-Sr-Ca-Cu-O SYSTEM

Masanori Kuroda and Michio Araki
Government Industrial Research Institute, Chugoku
Hiro-Suehiro, Kure, Hiroshima 737-01

The superconductivity of the Tl-Ba-Sr-Ca-Cu-O system was studied. The critical temperature (Tc) of this system was determined as 102 K by magnetic susceptibility measurements. Judging from the XRD measurement, the unit cell of this phase was estimated to be tetragonal with a=3.85A and c=12.3A. Furthermore, Rietveld analysis was performed in this system.

PHASE DIAGRAM AND CRYSTAL GROWTH OF Nd_2CuO_4 and Pr_2CuO_4 SYSTEM

Kunihiko OKA and Hiromi UNOKI

Electrotechnical Laboratory, Umezono 1-1-4, Tsukuba, Ibaraki 305 Japan

The phase diagram of Nd_2O_3-CuO system has been prepared and DTA measurements of other R_2CuO_4 (R=Pr, Sm, Eu, and Gd) have also been performed in air. Nd_2CuO_4 was found to melt incongruently at 1240 ℃. A liquidus line below 1240 ℃ is found in a composition range between 82 and 93 mol % CuO, suggesting that it is possible to grow a single crystal of peritectic Nd_2CuO_4 starting from CuO-rich composition of this range.

We are trying to grow single crystals of $(NdCe)_2CuO_4$, $(PrCe)_2CuO_4$, the electron-doped superconductor and other R_2CuO_4 by the slow-cooling, travelling-solvent floating-zone and top seeded solution growth method based on these obtained phase diagram and DTA measurements.

Magnetic and electric measurements are also being made on these single crystals and suggest that they come to be superconductive when annealed in Ar atmosphere at around 1000 ℃.

SUBSTITUTION EFFECTS ON SUPERCONDUCTIVITY AND STRUCTURE OF Nd_2CuO_4 WITH T'-Nd_2CuO_4 STRUCTURE

Katsuyoshi OH-ISHI, Masae KIKUCHI, Yasuhiko SYONO, Norio KOBAYASHI and Yoshio MUTO

Institute for Materials Research, Tohoku University, Katahira, Sendai 980, Japan

Substitutions of Nd^{3+} in Nd_2CuO_4 by different kinds of cations have been examined. Following three systems have been synthesized.

i) Na doped Nd_2CuO_4: $Na_xNd_{2-x}CuO_{4-y}$ for synthesis of p-type superconductor with T'-Nd_2CuO_4 structure.

ii) Ce doped Nd_2CuO_4: $Ce_xNd_{2-x}CuO_{4-y}$ for investigation of change of structure and confirmation of superconductivity.

iii) Ce and La doped Nd_2CuO_4: $Ce_{0.15}Nd_{1.85-x}La_xCuO_{4-y}$ for study of relation between Tc and Cu-O bond length within basal plane with electron concentration constant.

X-ray powder diffraction analysis, oxygen content, electrical resistivity and magnetic susceptibility measurements have been performed on the substituted sample. Hole or electron carrier concentration of the sample has been estimated on the basis of charge neutrality.

We consider changes of structure and carrier concentration of the sample in terms of ionic radius and valence and of oxygen content, and discuss their relation to superconductivity.

STABILITY OF T* AND T' PHASES IN $Nd_{1.4}Sr_{0.4}Ce_{0.2}CuO_{4-\delta}$

Takeshi Sakurai, Toru Yamashita, Sumio Ikegawa and H. Yamauchi
Superconductivity Research Laboratory,
International Superconductivity Technology Center
10-13 Shinonome 1-chome, Koto-ku, Tokyo 135 Japan

The T* phase in $(Nd,Sr,Ce)_2CuO_{4-\delta}$ has been found to be superconducting, having holes as charge carriers. On the other hand, another new-type superconductors have been discovered in $(Nd,Ce)_2CuO_{4-\delta}$ having T' phase with electrons as charge carriers. We have observed that $Nd_{1.4}Sr_{0.4}Ce_{0.2}CuO_{4-\delta}$ exhibits superconductivity after two different types of heat treatment, i.e., oxidizing and reducing heat treatment. The superconducting phases after heat treatment in oxidizing and reducing atmosphere are likely to be a T* and a T' phase, respectively. The T* → T' phase change requires that the O ions on the apices of $Cu-O_5$ pyramids in the T* phase are displaced by 1/2[100]. During this phase change, the Sr ions are required to diffuse out of the T* phase.

VALENCE STATE OF $Ba_{1-x}K_xBiO_3$ SUPERCONDUCTOR

Kazuhiro UEKI, Teruo SUZUKI*, Masae KIKUCHI, Masayasu NAGOSHI*
Norio KOBAYASHI, Ayako TOKIWA and Yasuhiko SYONO
Institute for Materials Research, Tohoku University,
Aoba-ku, Sendai 980, Japan
*Steel Research Center, NKK Corporation, Kawasaki-ku, Kawasaki 210, Japan

$Ba_{1-x}K_xBiO_3$ has either cubic or pseudocubic structure, and its lattice parameter decreases with increasing x. This decrease is probably related to Bi valence, because ionic radius of K ion is similar to Ba ion. However, the plot of lattice parameter vs. Tc discontinuously decreased around x=0.3, indicating relation to the pseudocubic-cubic transition reported by Hinks et al. This composition is close to Tc limit of x=0.35~0.4.

To see the effect of Bi valence on the lattice parameter and superconductivity, we synthesized $Ba_{0.6}K_{0.4}BiO_{3-\delta}$ specimens by various heat treatments at different atomspheres. Superconductivity appeared for the specimens whose lattice parameter is below 4.31A, where Tc took a maximum value of 28K. Valence state of Bi ions observed in XPS measurement will be discussed in terms of oxygen content.

CGS, THE CRYSTAL STRUCTURE GRAPHICS DISPLAY SYSTEM, FOR SUPERCONDUCTING MATERIALS

S.Ono*, H.Hayakawa*, K.Tanabe*, K.Naito**, Y.Imasato**
* National Chemical Laboratory for Industry, 1-1 Higashi, Tsukuba, 305 Japan
** FACOM-HITAC LIMITED, 6-2 Sanbancho, Chiyoda-ku, Tokyo, 102 Japan

Although there are several molecular structure graphics systems which have been developed to display organic molecules or biomolecules, they are not suitable for presenting inorganic crystal structures. A new 3-dimensional crystal structure graphics system, CGS, is under development in order to make crystal structures understood more easily. The CGS program can be run on a host computer, FACOM M780 with a graphics terminal, COMTEC DS301B.

The input data specify space group symbols, unit cell parameters, radii and color of atomic sphere displayed, bonding information, etc. Skeleton and ball & stick representations can be selected. The color and thickness of bonds can be selected by the bonding information data, which makes understood easily special features of inorganic structures, such as the layer stacking or the coordination state of special sites. Display of more than one unit cell is sometimes needed to understand the structural characteristics and such facility has been developed in this system.

Conversion of the program to Sun workstation is now under way.

INTERFACE STUDIES OF Y-Ba-Cu-O AND Bi-Sr-Ca-Cu-O FILM SURFACES CLEAVED AT 77K IN VACUUM WITH IN-SITU EVAPORATED GOLD

I. Takeuchi, J. S. Tsai, H. Tsuge, N. Matsukura, S. Miura, Y. Kojima, and S. Matsui

Fundamental Research Laboratories, NEC Corporation,
Tsukuba, Japan

We have been exploring the possibility of preparing relatively "clean" film surfaces of high-temperature oxide superconductors, free of unavoidable natural degradation present at the top layer, that can be used to form contacts with other materials such as gold.

Single-crystal films of RF sputtered Y-Ba-Cu-O (Tc~75K) and as-deposited RF sputtered Bi-Sr-Ca-Cu-O (Tc~80K) were used for the present study. Films are cleaved in vacuum of $1x10^{-7}$ Torr while the film substrate is cooled down to 77K. In-situ evaporation of Au is done on the uncovered cross-sectional surface of the films, and the electrical properties of the interface contacts were studied. The effect of subsequent rapid thermal annealing on the contacts are also studied. This work was supported by NEDO under the management of FED.

HALL EFFECT MAGNETORESISTANCE IN EPITAXIALLY GROWN $YBa_2Cu_3O_{7-y}$ FILM.

T. R. NICHOLS, K. MURATA, H. ITOZAKI,* T. KOMAZAKI AND Y. NISHIHARA,
Electrotechnical Laboratory, Umezono, 1-1-4, Tsukuba Ibaraki 305, Japan.
*Sumitomo Electric Industries, Koya-Kita1-1-1,Itami, Hyogo 664, Japan

We present measurements of the Hall coefficient ($H//c$) and resistivity in the ab plane of an epitaxially grown $YBa_2Cu_3O_{7-y}$ thin film. Longitudinal magnetoresistance is less than $\Delta\rho/\rho = 10^{-4}$ in applied magnetic fields($//c$) up to 5 T in all temperature ranges between room temperature and T_c.

The Hall coefficient varies as $A+B/T$ and is smaller in value to that obtained by other groups on single crystals. In comparison, the measured resistivity was also found to be correspondingly smaller.

Subsequently, the resultant mobility values are in the same range as published data. The mobility was found to vary strictly as $T^{-1.5}$. A proposed scattering mechanism to account for the observed temperature dependence of mobility will be presented.

HALL EFFECT IN OXIDE SUPERCONDUCTORS HAVING FLUORITE-TYPE LAYERS

Sumio Ikegawa, Michikazu Kosuge, Takahiro Wada, Ataru Ichinose, Yuji Yaegashi, Kouichi Nakao, Toru Yamashita, Takeshi Sakurai and H. Yamauchi

Superconductivity Research Laboratory
International Superconductivity Technology Center
10-13 Shinonome 1-Chome, Koto-ku, Tokyo 135, Japan

In the last ten months, a new type of oxide superconductors which have fluorite-type layers in their crystal structure has been discovered. It includes $(Nd,Ce)_2CuO_{4-y}$ (T'-phase), $(Nd,Ce,Sr)_2CuO_{4-y}$ (T^*-phase), and $(Ln,Ce)_4(Ba,Sr,Ln)_4Cu_6O_z$:Ln=Nd, (La,Gd). We have investigated the Hall effect, especially its dependence on temperature, in the ceramic samples of those superconducting compounds. Measurements were performed for bar-shaped samples using a 6T superconducting solenoid at temperatures between 4 and 300 K.

The sign of the Hall coefficient (R_H) was negative for $(Nd,Ce)_2CuO_{4-y}$, and positive for $(Nd,Ce,Sr)_2CuO_{4-y}$ and $(Ln,Ce)_4(Ba,Sr,Ln)_4Cu_6O_z$. The magnitude of R_H for all the three compounds exhibits a broad peak around 120-150 K with respect to temperature. It is contrary to the case of K_2NiF_4-type superconductors and 1:2:3 superconductors, where R_H increases monotonically with decreasing temperature. The difference may arise from the fluorite-type layer or Ce contained in the three compounds. In $(Ln,Ce)_4(Ba,Sr,Ln)_4Cu_6O_z$, the hole density derived from R_H is smaller than that derived from chemical formula and oxygen analysis. This suggests that all the holes introduced in the Cu-O plane by chemical doping are not mobile in this compound. Comparison of the temperature dependence of R_H between different kinds of crystal structure of copper-based oxide superconductors will be made.

THERMOELECTRIC POWER IN THE NORMAL STATE OF HIGH-Tc SUPERCONDUCTORS

Ruan Yaozhong Wang Ruiping
(Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui, P.R.China)

The thermoelectric power of ceramic oxide superconductors such as $YBa_2Cu_3O_{7-y}$, $Tl_2Ba_2Ca_2Cu_3O_y$, and $Bi_{1.5}Pb_{0.5}Ca_2Sr_2Cu_3O_y$ has been precisely measured over the temperature range 77-300K. It is found that the thermoelectric power is positive and there is a peak above the transition temperature Tc for all samples. In high temperature range, the temperature dependence of thermoelectric power can be expressed $S=AT+B/T$. We suggest that phonon-drag thermopower can not neglect in high temperature range and there exists the electron-phonon interaction for high Tc superconductors and the peak above Tc is a phonon-drag peak that is truncated by the onset of superconductivity. According to the data of thermoelectric power, we estimate the Fermi energy for these materials, they are 1.05ev, 2.98ev and 3.24ev for $YBa_2Cu_3O_{7-y}$, $Tl_2Ba_2Ca_2Cu_3O_y$ and $Bi_{1.5}Pb_{0.5}Ca_2Sr_2Cu_3O_y$ respectively.

UNUSUAL PHYSICAL PROPERTIES OF $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ FAMILY MATERIALS

A. MAEDA, T. YABE, S. TAKEBAYASHI, M. HASE, K. NODA and K. UCHINOKURA
Department of Applied Physics, The University of Tokyo, Tokyo, JAPAN

$Bi_2Sr_2Ca_{n-1}Cu_nO_y$ family forms a broad range of materials which have the superconducting transition temperature T_C between 0 K (semiconductor or normal metal) and 120 K with various number of CuO_2 layers in a unit cell. We prepared single-phase polycrystalline samples, highly oriented thin films, single crystals of these materials doped by various cations. After the sufficient characterization the following subjects were investigated. (1) The phase diagram of T_C *versus* hole concentration of single layered (2201), double layered (2212), and triple layered (2223) systems doped with various cations (2) Hall effect, infrared optical reflection, and the static spin susceptibility in normal state of these samples (3) the effect of substitution for Cu by other 3d metals (Fe, Ni, Co and Zn) which introduce both in-plane disorder and extra magnetic moment (3) surface impedance at 24 GHz in order to estimate the energy gap in superconducting state (4) noise in conductivity in normal state and around T_C. Superconductivity was found to depend at least on three independent factors; the number of Cu oxygen layers in a unit cell, hole concentration, in-plane disorder introduced by doped 3d ions. A semiconductor (with antiferromagnetic ordering) - high T_C superconductor - normal metal transition was confirmed to exist in Bi-compounds. Furthermore, many highly anomalous feature have been found in normal state of these materials, which suggests that the normal state of these materials is far from that of the conventional metal. The implications will be discussed in terms of several models for high-T_C superconductivity.

HOLE CONCENTRATION DEPENDENCES OF T_c IN CUPRATE OXIDE SUPERCONDUCTORS

K. Takita, H. Akinaga, T. Ohshima and Y. Orimoto

Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki, 305 Japan

By the changing of two parameters of x and δ , in $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ ($-0.5 \leq \delta \leq 0.2$, $0 \leq x \leq 0.4$), it is found that the superconducting transition temperature T_c is determined uniquely by the hole concentration p_H, where p_H is the effective hole concentration deduced from the Hall coefficient R_H ($p_H=V_o/R_He$: V_o is the volume of the unit cell.). p_H shows almost the same value to $2p_s$ which is a mobile hole concentration in two sheets of CuO_2 plane deduced from chemical analysis. Furthermore, T_c increases with p_H almost linearly up to 95K showing a contrast to the case of $La_{2-x}Sr_xCuO_4$.

In this paper, results of hole concentration determination in Nd-Ca-Ba-Cu-O system, 2-2-1-2 and 2-2-2-3 phase Bi systems will be also presented and are discussed with emphasis on the universal relation between T_c and hole concentration.

Superconducting properties of $(GdCe)_4(LaBaSr)_4Cu_6O_{18.8}$

T.Kaneko, T.Wada, A.Ichinose, Y.Yaegashi,
S.Ikegawa and H.Yamauchi
Superconducting Reseach Laboratory,
International Superconductivity Technology center,
10-13 Shinonome 1-Chome, Koto-ku, Tokyo 135 Japan

We have investigated the superconducting properties of a 40 K class superconductor, $(GdCe)_4(LaSrBa)_4Cu_6O_{18.8}$, by transport and magnetization measurements. The sample showed metallic temperature dependence of resistivity down to the superconducting transition temperature of 38 K and a sharp superconducting transition . The Meissner onset temperature, T_c^{mag}, was 38 K and the superconducting volume fraction was about 30 % of a full Meissner effect. The lower critical field, $H_{c1}(0)$, estimated from the field dependence of the magnetization was 110 Oe. If we adopt midpoints of the resistive transition as T_c's in the magnetic field, the upper critical field, $H_{c2}(0)$, was obtained to 20.7 T. The superconducting materials parameters were derived using these values for $H_{c1}(0)$ and $H_{c2}(0)$: κ =62.3, ξ (0)=40 Å, λ (0)=2500 Å, $H_c(0)$=2.4 kOe and γ =16.8 mJ/moleK^2. The magnetic properties in the nomal state of the sample were also investigated. The magnetic susceptibility data were fitted well with the Curie-Weiss law. The magnitude of the measured magnetic moment was 7.97 μ_B being in good agreement with the theoritical value of a 7.94 μ_B for a Gd^{3+} free ion.

CORRELATION BETWEEN Tc AND DENSITY OF STATES IN LAYERED OXIDE-SUPERCONDUCTORS

H. IHARA, T. SIMOMURA, R. SUGISE, N. TERADA,
M. JO, Y. KATO, M. TOKUMOTO AND M. HIRABAYASI,
Electrotechnical Laboratory, 1-1-4 Umezono, Tukuba, Ibaraki 305 Japan.

Empirical rules on Tc are very important for searching new high Tc superconductors. Multi-CuO layer superconductors: $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$, $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ and $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ families (n=1 ~ 5), have a strong correlation between Tc and the number of CuO layers (n). The empirical rule: Tc = an exp(- bn) suggests an empirical formula of $Tc = A\, N(E_F) \exp(- BN(E_F))$ between Tc and the density of states ($N(E_F)$). On the other side, the general theory on phase transition phenomena rather suggests another empirical formula of $Tc = A\, N(E_F) \exp(- B'/N(E_F))$. The former formula is, however, consistent with the empirical rule between Tc and carrier concentrations.

We have examined the empirical rules by measuring the density of states of several layered CuO superconductors. The density of states of superconductors were observed by photoelectron spectroscopic and magnetic susceptibility measurements.

SUPERCONDUCTING PROPERTIES AND ESR OF Mn-DOPED $YBa_2Cu_3O_{7-x}$

M. Kaise, M. Mizuno, C. Nishihara, H. Nozoye and H. Shindo

Division of Basic Research, National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305, Japán

Materials of partially substituted copper with manganese in high-Tc $YBa_2Cu_3O_{7-x}$ were prepared from Y_2O_3, $BaCO_3$, CuO, and $Mn(NO_3)_2$ mixtures by heat treatment in air (Room temp. ---→ 940 °C <12 hr> ---→ 520 °C <6 hr> ---→ Room temp.). It is found that Tc decreases with an increase of the Mn concentration, but the superconductivity is not destroyed even at 2 percent substitution and Tc was 78K (assumed invariable composition of Y, Ba, Cu and Mn from the starting materials).

The ESR of unsubstituted and Mn substituted $YBa_2Cu_3O_{7-x}$ in normal and superconducting phase has been measured at room temperature. No appreciable signal by paramagnetic species was observed from any prepared samples without any treatment. This fact shows that neither Cu nor Mn in all samples are present as isolated divalent cations. However, all powder samples after manual grinding have shown similar ESR powder spectrum of para-magnetic species ($S=1/2$) with rohmbic g-tensor ($g_x = 2.049$, $g_y = 2.122$, $g_z = 2.234$) and no resolved hyperfine structure. The signals are assigned to Cu^{2+} in distorted crystal field and they have been produced on the surface of the crystallites by mechanical force of grinding.

ESR STUDY ON HIGH Tc SUPERCONDUCTING OXIDES

Y.YAMADA, K.SUGAWARA, and Y.SHIOHARA
Superconductivity Reserch Labolatory, ISTEC, Tokyo, Japan

We have prepared samples of superconducting oxides by means of conventional ceramic powder processing, in which parts of Cu ions were substituted by other metallic ions, and the variation of signals of electron spin resonance(ESR) due to substituting elements has been investigated. Al, Zn, Ni, Mn, or V was used as a substituting element for 3% Cu ions. Each of samples substituted by Al, Zn, Ni, and V has similar ESR signals. These signals are considered to be originated from Cu ions. The numbers of Cu ions responsible for the ESR are less than about 1% of total number of Cu ions, and they gradually increase with keeping samples in air. In contrast, for samples substituted by Mn, a broad signal of Mn ions was almost independent of temperture. However, the absorption intensity, i.e. spin susceptibility, shows a weak peak at about 300K, and decreases with decreasing temperature and disappears at about 85K. This result indicates that Mn ions become in a spin singlet state with decreasing temperature, which might be related to a spin state of Cu ions.

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INTERACTIONS AMONG Gd AND Cu-2 IN $GdBa_2Cu_3O_y$ COMPOUNDS

F.NAKAMURA, K.SENOH, T.TAMURA, S.NAKATA, [+]Y.OCHIAI and Y.NARAHARA
Institute of Physics, and [+]Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

In 90K superconductor $GdBa_2Cu_3O_y$ compounds, superconductivity coexists with Gd antiferromagnetic ordered state below 2.3 K. The crystal structures and the susceptibilities of normal phase indicate that magnetic interactions among Gd ions should be expected the dipole-dipole interaction. The Néel temperature (T_N) is calculated from this interaction to be about 1.5 K. However, the observed T_N(2.3 K can not explain with only this interaction. We performed 9 and 24 GHz electron-spin-resonance (ESR) studies for $GdBa_2Cu_3O_y$ compounds. The results of oxygen concentration dependence in g value indicate that Gd ions interact with Cu-2 planes. From the frequency dependence in linewidth and lineshape, we estimated an exchange type and dipole type interactions. Interesting Gd linewidth behaviors for $GdBa_2(Cu_{1-x}M_x)_3O_y$ (M= Ni, Co and Fe) compounds are observed. We discuss the interactions among Gd ions and Cu-2 planes and behaviors of doped ions.

ESR, NONRESONANT MICROWAVE ABSORPTION AND STATIC MAGNETIC SUSCEPTIBILITY IN Tl-Ba-Ca-Cu-O SYSTEM

Yoshikazu Hayashi, Kengo Adachi[†], Katsutoshi Iwahashi[†], Hideo Shibayama[†], Minoru Fukui[#] and Tetsuo Fujita[†]
Materials Science, University of Osaka Prefecture, Sakai, Osaka 591 Japan
[†]Department of Physics, Nagoya University, Chikusa ku, Nagoya 464 Japan
[#]Nakanihon Automotive College, Sakahogi cho, Kamo-gun, Gifu-ken, 505 Japan

The electron spin resonance (ESR) of Cu^{2+} ions has been detected in the fine powder of the Tl-Ba-Ca-Cu-O sytem having three sheets of a CuO_2 plane. Two kinds of ESR signals have been detected. One of them is broad isotropic and the other is anisotropic. Both of these signals disappear at 124K which corresponds to the transition point T_c of the superconductivity. Origins of these signals are not considered to be impurities. Nonresonant absorption near zero magnetic field is greatly enhanced at T_c. Below T_c, several structures appear in the derivative curve of the nonresonant microwave absorption. Because the sample consists of fine grains coupled each other by the Josephson effect, not only the behavior of flux lines but also the magnetic field dependence of the critical current of the Josephson effect are considered to be responsible for the origin of these structures. The temperature and the magnetic field dependence of the static magnetic susceptibility are presented and the relation with the results obtained in the microwave experiment is discussed.

OPTICAL STUDY OF THE ELECTRONIC STATES IN HIGH-T_c CUPRATES

Setsuko TAJIMA and Shoji TANAKA
Superconductivity Research Laboratory, ISTEC,
Shinonome 1-10-13, Tokyo 135, JAPAN
Tatemi IDO and Shin-ich UCHIDA
Department of Applied Physics, University of Tokyo,
Hongo 7-3-1, Tokyo 113, JAPAN

In order to discuss the mechanism of high-T_c superconductivity, it is important to know what kind of elementary excitations are observed and how they correlate with the superconductivity in these materials.

In this study the optical reflectivity spectra of $La_{2-x}Sr_xCuO_4$ single crystals were measured for various Sr-content, covering the energy range from far-infrared to ultraviolet. When the system changes from insulator to superconducting metal with Sr-doping, the spectral weight moves from the charge-transfer-excitation peak at 2eV to the lower energy spectral part, another peak appearing in the conductivity spectrum lower than 1eV and growing into a free carrier plasma conductivity. This is supposed to be a unique structure for the high-T_c cuprates in the crossover region between Mott-Hubbard insulator and Fermi liquid metal, although the origin of the lower energy conductivity peak yet remains a question.

Together with the compositional dependence mentioned above, temperature dependence and anisotropy of the spectra are also discussed.

^{57}Fe AND ^{57}Co MÖSSBAUER STUDIES OF HIGH-T_c Y-Ba-Cu OXIDES

S.Nasu, M.Yoshida, Y.Oda, K.Ueda*, T.Kohara*, T.Shinjo**, K.Asayama, F.E.Fujita, S.Katsuyama***, Y.Ueda*** and K.Kosuge***: Department of Material Physics, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan. *Himeji Institute of Technology, Himeji, Hyogo671-22, Japan. **Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611, Japan. ***Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan.

Utilizing the ^{57}Fe absorption and ^{57}Co emission Mössbauer spectroscopy, chemical and physical properties of Fe-doped and Co-doped $YBa_2Cu_3O_{7-y}$ oxide superconductors have been investigated. Mössbauer spectra obtained from the doped specimens consist of mainly four components. Hyperfine interaction parameters do not depend on the dopant concentration and the heat treatments, but the relative intensities of the each components depend largely on the oxygen concentration of the specimens. In order to clarify the magnetic and site occupation problems of Fe and Co atoms at two different Cu sites in these 1-2-3 compounds, some specimens are heat-treated in different ways and some are prepared to have a strong texture along the c-axis. It is found that Fe and Co atoms mainly substitute at Cu1 chain sites, while a small portion of Fe atoms (about 20% of total dopant content) occupy the Cu2 plane sites indicating an antiferromagnetic long-range order in oxygen deficient compounds. Neel temperature of Fe at Cu2 plane sites in oxygen deficient Fe-doped specimen is 423 K and the direction of their magnetic moment is normal to the c-axis. Fe atoms at Cu1 chain sites show magnetically broadened Mossbauer spectra at low temperatures irrespective of the superconducting or non-superconducting state. The essential features of magnetically broadened components rising from Fe at Cu1 sites are not affected but the strength of the magnetic interaction at Fe in Cu2 is remarkably weakened by the existence of superconductivity.

ELECTRONIC STRUCTURE AND MIDINFRARED EXCITON BANDS OF CUPRATE SUPERCONDUCTORS

Jiro TANAKA, Masaaki SHIMIZU, Satoru MIYAMOTO, Chizuko TANAKA and Koji KAMIYA*
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464-01, Japan
* Institute for Molecular Science, Okazaki, 444, Japan

Electronic band structure of cuprate superconductor is important to understand the mechanism of Cooper pair formation. We used a new theoretical method and interpreted the midinfrared exciton bands as the interband electronic transitions between the bands composed of antibonding MO of O(2px) and O(2py) orbitals of $(CuO_4)6-$ cluster ion.

We considered the CuO_2 plane common to cuprate superconductors is composed of $(CuO_4)6-$ ion and $(Cu)2+$ ion. The molecular orbitals (MO) of $(CuO_4)6-$ ion are calculated by the ab initio UHF SCF MO method. In the CuO_2 plane, the highest occupied MO (HOMO) is antibonding combination of π-type O(2px,y) orbitals, since $Cu(3d_{x^2-y^2})$-$O(2p\sigma)$ type HOMO of isolated $(CuO_4)6-$ ion comes down to lower energy region by the interaction with vacant orbitals of surrounding $(Cu)2+$ ions. The energy band structure is calculated by tight binding approximation with each MOs.

Reflection spectra of single crystals of $La_{1-x}Sr_xCuO_4$, $Bi_2(Sr,Ca)_3Cu_2O_{8+x}$ and $Tl_2Ca_2Ba_2Cu_3O_z$ are measured from far IR to UV region. Optical conductivity spectra of these crystals on the (001) plane consists of Drude term and several exciton bands at 0.05 - 0.5 eV region. These exciton bands are explained as interband transitions to the π-holes of O(2px,y) antibonding type HOMO band from the degenerate O(2px) and O(2py) type next HOMO bands. Dielectric functions are determined from the optical spectra, which indicate importance of electron exciton interaction for pair formation mechanism.

RAMAN SCATTERING SPECTRA OF $NdBa_2Cu_3O_x$ SINGLE CRYSTALS

MASASHI YOSHIDA, SATOSHI GOTOH, TUTOMU TAKATA and NAOKI KOSHIZUKA
SUPERCONDUCTIVITY RESEARCH LABOLATORY, ISTEC, TOKYO 135, JAPAN

Raman scattering from $NdBa_2Cu_3O_x$ single crystals with superconductive transition temperature Tc around 60K have been studied. Scattering lines due to five Ag symmetry phonons have been observed at 136, 163, 316, 442 and 496 cm^{-1} among which the 316cm^{-1} line is strong in the (a,a) configuration while the 442 and 496cm^{-1} lines are strong in the (c,c) configuration. This polarization dependence is similar to that of $YBa_2Cu_3O_x$. In the (a,a) configuration there are three broad peaks around 580, 1160 and 2500cm^{-1}. The 1160cm^{-1} peak has been identified as the overtone of the 580cm^{-1} peak. These lines could be associated with the stretching vibration mode of the oxygen atoms in the Cu-O planes which becomes Raman allowed in the single phonon scattering by the oxygen deficiency, though in $YBa_2Cu_3O_x$ the 1200cm^{-1} peak was assigned to the single spin flip scattering. The 2500cm^{-1} peak is assigned as the 2-magnon line which has been observed also in $YBa_2Cu_3O_x$ with Tc below 60K. In the (c,c) configuration, on the other hand, 2-magnon line has not been observed but up to 3-phonon scattering lines of the 496cm^{-1} phonon have been observed.

OPTICAL PROPERTIES OF $Ln_{2-x}Ce_xCuO_4$ (Ln=Pr,Nd and Sm) SINGLE CRYSTALS

IZUMI TOMENO, MASASI YOSHIDA, KAZUTO IKEDA, TSUTOMU TAKATA, KEISI TAI, and NAOKI KOSHIZUKA

SUPERCONDUCTIVITY RESEARCH LABORATORY, ISTEC, TOKYO 135, JAPAN

Raman scattering studies were made for $Ln_{1-x}Ce_xCuO_4$ (Ln=Pr,Nd and Sm) single crystals in the frequency range between 100 and 5000 cm^{-1}. For parent crystals, two-magnon broad peaks were observed at 2700 cm^{-1}. Two-magnon scattering exists in $Pr_{1.85}Ce_{0.15}CuO_4$ at room temperature, although their peaks are suppressed considearbly. These observations are interpreted in view of the relationship between antiferromagnetism and superconductivity. The 580 and 1160 cm^{-1} peaks observed in (a,a) polarization are ascribed to the disorder-induced one and two phonon modes related with oxygen stretching in the Cu-O planes. These features are similar in behavior to those for $NdBa_2Cu_3O_7$ single crystals.

RAMAN MAPPING OF Bi-Sr-Ca-Cu-O FILMS

Toshimasa Suzuki, Kazutoshi Kainuma, *Takeshi Kawai,
Katsuyoshi Hotta and Haruo Hirose

Nippon Institute of Technology, Miyashiro, Japan
*Chichibu Fuji, Ogano, Japan

High-Tc rich phase and low-Tc rich one of Bi-Sr-Ca-Cu-O films have been successfully classified spatially by micro-Raman spectroscopy mapping.

Samples were grown on (100)MgO substrates by spray pyrolysis method using naphtanic salts of Bi, Sr, Ca and Cu in the atomic ratio of 1:1:1:2 as raw materials. Sample A, which was sintered at 950°C for ten minutes, showed single step behavior in temperature dependence of electrical resistivity and zero resistivity temperature of 68K. Surface morphology of this sample showed c-plane oriented plate-like crystals and distributed granular crystals. Raman spectra of these crystals were measured and it was found that the granular crystals are high-Tc rich phase and plate-like crystals are low-Tc rich one. On the other hand, sample B, which was sintered at 970°C for ten minutes, showed two step behavior in resistivity indicating the existence of no small high-Tc phase, although the zero resistivity temperature was lowered to 50K.

Raman intensity mapping of 461cm^{-1} and 548cm^{-1} lines of these samples was obtained using an Ar^+ laser beam of 2$\mu m\phi$ in diameter in backscattering geometry at room temperature. Distributions of 548cm^{-1} and 461cm^{-1} lines of sample A were well corresponding to that of plate-like crystals and granular ones respectively. Moreover the density of intense part of 461cm^{-1} line of sample B increased. 461cm^{-1} line appears in (2212) phase and in the mixture of (2212) and (2223) phases. Taking into account the shape of R-T curve, it was concluded that the parts where 461cm^{-1} line is intense are corresponding to high-Tc (2223) phase.

PHONON ECHOES IN SUPERCONDUCTING POWDERS OF Tl-Ba-Ca-Cu-O AND (Bi,Pb)-Sr-Ca-Cu-O

H. Nishihara[1], K. Hayashi[2], M. Takano[3], K. Kishio[4], T. Ohtani[2], K. Kajimura[5], Y. Okuda[6], T. Tamegai[4] and K. Motoya[7]
Ryukoku Univ.[1], Okayama Univ. of Sci.[2], Kyoto Univ.[3], Univ. of Tokyo[4], Electrotechnical Lab.[5], Tokyo Inst. of Tech.[6] and Saitama Univ.[7], Japan

Study of rf phonon echoes observed in the superconducting state of powders of high-T_c oxide $YBa_2Cu_3O_{7-\delta}$ /1/ has been extended to the new oxide systems of Tl-Ba-Ca-Cu-O and (Bi,Pb)-Sr-Ca-Cu-O. The coupling mechanism between rf fields and acoustic modes is confirmed to be different from that in usual phonon echoes judging from the sudden disappearance of the echoes at each T_c of the new oxides. Mechanisms of the signal enhancement in the observation of phonon echoes are proposed for the superconducting state of strongly anisotropic superconductors or for the superconductors in which a pinning of the fluxoids to each particle is sufficiently strong. The temperature dependences of the echo intensity and the echo decay rate T_2^{-1} are found to be not smooth functions of temperature T in the systems of Tl-Ba-Ca-Cu-O and (Bi,Pb)-Sr-Ca-Cu-O, but they have anomalies at the temperatures which seem to be low T_c's of the coexisting second superconducting phases in a powdered specimen. This properties of the phonon echoes provide a new way of characterizing powders of high-T_c oxides in high quality.

/1/ H. Nishihara, K. Hayashi, Y. Okuda and K. Kajimura, Phys. Rev. B39, 7351 (1989)

ULTRASONIC, VIBRATING REED AND X–RAY STUDY OF THE STRUCTUAL PHASE TRANSITION IN SINGLE CRYSTAL $La_{2-x}Sr_xCuO_{4-y}$ HIGH T_c SUPERCONDUCTOR

T.Laegreid, Wu Ting, O.–M.Nes, M.Slaski, E.Eidem, E.J.Samuelsen, K.Fossheim and Y.Hidaka[1]
Division of Physics, The Norwegian Institute of Technology, and Division of Applied Physics – SINTEF, N–7034 Trondheim, Norway
1) Nippon Telegraph and Telephone Corporation, Tokai, Ibaraki 319–11, Japan

Measurements of the elastic and structural properties performed on a single crystal $La_{2-x}Sr_xCuO_{4-y}$ high–T_c superconductor are presented. The longitudinal ultrasonic measurements were performed at 13MHz. A strong decrease in the sound velocity and a sharp peak in the sound attenuation is found and associated with a softening of the lattice. Distinct change in the vibrating reed response is found in the same temperature range. These strong anomalies in the elastic properties are ascribed to the tetragonal to orthorhombic phase transition at $T_0 \simeq 255K$. X–ray intensity measurements support these observations. The interesting possiblity of an additional low temperature structural transition is also investigated.

DEGRADATION, BY MECHANICAL GRINDING, AND RECOVERY, BY ANNEALING, IN THE SUPERCONDUCTING PHASES OF THE Bi-Sr-Ca-Cu-O SYSTEM

Tsuneyuki KANAI, Tomoichi KAMO and Shin-Pei MATSUDA
Hitachi Research Laboratory, Hitachi Ibaraki, 317 Japan

It has been found that mechanical grinding may degrade superconducting phases to non-superconducting phases; i.e., a sample with 73 vol% of the high-Tc phase, 18 vol% of the low-Tc phase and 8 vol% of the non-superconducting phase resulted in a sample with 98 vol% of the non-superconducting phase after grinding for 62 min. X-ray analysis showed that the initial cleavage fracture of the high-Tc phase in the (001) planes occurred more easily than that of the low-Tc phase by mechanical grinding. The (001) fracture gradually changed to a more the isotropic fracture on prolonged grinding.

It was also found that the degraded sample did not recover easily to the initial conditions; i.e., the ground sample shows the high-Tc phase of only 30 vol% after annealing for 62 min. However, the volume of the high-Tc phase of the amorphous samples free from the high-Tc phase was 60 % in the same annealing conditions. Therefore, a process which includes crystal grinding, causing the degradation of the superconducting phases, is not considered appropriate for fabricating practical superconducting wires or sheets.

ELECTRON MICROSCOPIC STUDIES OF SHOCK LOADING EFFECTS ON HIGH Tc SUPERCONDUCTOR

Masae Kikuchi, Yasuhiko Syono, Masayasu Nagoshi*, Ayako Tokiwa, Eiji Aoyagi, Teruo Suzuki*, Keiji Kusaba and Kiyoto Fukuoka

Institute for Materials Research, Tohoku University, Katahira, Aoba-ku, Sendai 980, Japan
*Steel Research Center, NKK corporation, Kawasaki-ku, Kawasaki 210, Japan

Shock loading effects on high Tc oxides, La-Sr-Cu-O, Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O systems, were studied for the pressure range 5-15GPa by TEM observation and measurements of resistivity and magnetic response. The structure defects induced by shock loading are closely related to the structure and bonding type of materials. Shock deformation in $La_{1.85}Sr_{0.15}CuO_4$ with K_2NiF_4 type structure is due to dislocation with crossed networks. $YBa_2Cu_3O_7$ with the triple perovskite structure shows stacking fault and mechanical twinning by shock loading. Deformation textures of $Bi_2Sr_2CaCu_2O_8$ with layered structure are quite different from those in the La- and Y-systems. The samples shocked to 5-10GPa shows very unique texture of kink bands which are characteristic for deformation structure in mica-like compounds. The kink bands are observed only for incident beam is taken with perpendicular to shock direction.

$Bi_2Sr_2CaCu_2O_8$ shocked to 5GPa shows considerable degradation of Tc compared with that of other superconducting oxides. Increase of pressure range to 7.8GPa completely destroy the superconductivity. Annealing of the shocked specimen at 870°C in air for 10 hours recovers superconductivity with improvement in Tc. The same treatment of unshocked specimen little affect Tc. The deformation due to kinking is probably the origin of easy degradation superconductivity in the shocked Bi-system. The comparison of shocked and subsequent annealed specimen of Bi-system studied by TEM observation will be presented to explain the characteristic changes of behavior.

SUPERCONDUCTING TRANSITION OF 2D TWO-BAND SYSTEMS WITH EXCHANGE-LIKE INTERACTION

Kunihiko YAMAJI, Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba 305, Japan

SUPERCONDUCTING TRANSITION OF 2D TWO-BAND SYSTEMS WITH EXCHANGE-LIKE INTERACTION
Kunihiko YAMAJI, Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba 305

The exchange-like interaction by which BCS pairs are scattered between two bands is known to be divergently intensified through a process expressed by ladder diagrams in 1D two-band systems. We have found that this intensification is divergible also in the case of 2D two-band systems with electron and hole pockets. In such systems interband polarization function is analytically obtained and has a peak for wave number equal to the difference of the two Fermi wave numbers. This peak can lead to the divergence of the ladder-diagram process for important wave numbers, leading to s-wave superconductivity. An equation for T_c taking account of this effect is derived and numerically solved. With no other pairing mechanism T_c becomes finite and large, exceeding 100 K, despite sizable U when the ladder-diagram process is close to or has the divergence. This mechanism is argued to be substantiated in the high-T_c oxides. Competition with an SDW transition is also discussed.

ELECTRONIC STATES OF Cu_nO_m CLUSTERS BY DV-Xα CALCULATION

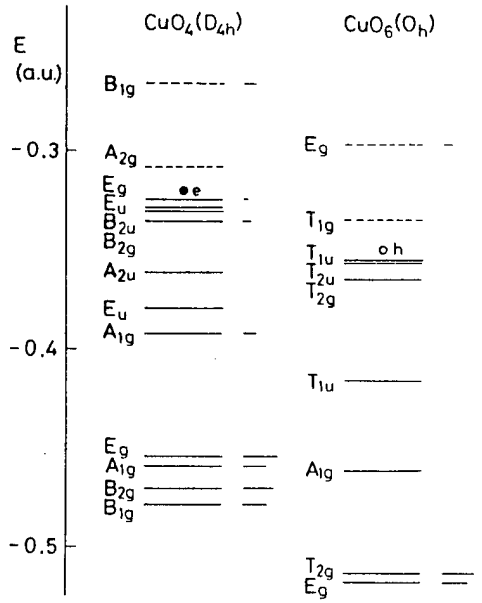
Tsuyoshi Yamaguchi and Nobuhisa Fujima
Faculty of Engineering, Shizuoka University, Hamamatsu 432, Japan

Electronic states of neutral CuO_4, CuO_6, Cu_4O_{12} and Cu_4O_{20} clusters are calculated by the DV-Xα method.

Valence energy levels of CuO_4 and CuO_6 are shown in the figure, where full and dashed lines represent the occupied and unoccupied levels, respectively. Mulliken charge population of the 3d-electron is represented by the length of the line on the right hand side.

The Cu 3d-levels have the lower energies of the valence band. The O 2p-levels which are hybridized with the 3d-levels have the higher energies. The Fermi level of CuO_4 and CuO_6 is E_g or T_{1u} where an electron or a hole is located, respectively.

The resultant electron configuration is $Cu{:}3d^{9.11}5_s^{0.38}5_p^{0.38}$ $O{:}2p^{4.28}$ for CuO_4 and $Cu{:}3d^{9.02}4_s^{0.30}4_p^{0.42}$ $O{:}2p^{4.21}$ for CuO_6. Calculation shows that the Cu ionicity and the number of 3d-hole increase for larger clusters.



FERMIONS AND SOLITONS IN THE $O(3)$ NON-LINEAR SIGMA MODEL IN $2+1$ SPACE-TIME DIMENSIONS

(Work Done in Colloboration with Sebastian Doniach)

The field theory limit of antiferromagnetism with holes is described using the O(3) non-linear sigma model. The minimal coupling to the spin-waves gives a Pauli term that couples the hole charge density to the topological charge density for solitons. This term leads to drastic consequences; an attractive potential for holes and solitons, spin-charge coupling for the holes and zero momentum modes. The zero momentum modes are exact non-perturbative solutions to the full coupled equations of motion for spin-waves and holes. The effect of a Chern-Simons term, connections to other mean-field approaches and the quantum boundstate problem are discussed. If the zero modes are the states of lowest energy, then the holes in this field theory limit are attached to skyrmions. This provides an analytic expression for the Spin Bag in terms of the continuum Non-Linear Sigma Model.

Purushotham Voruganti
DEPARTMENT OF PHYSICS

DIRECT OBSERVATION OF SUPERCONDUCTING MAGNETIC FLUXONS USING ELECTRON HOLOGRAPHY

Shuji Hasegawa, Tsuyoshi Matsuda, Junji Endo, Akira Tonomura and Ryozo Aoki*

Advanced Research lab., Hitachi Ltd., Kokubunji, Tokyo 185 JAPAN
* Faculty of Eng., Osaka Univ., Suita, Osaka 565 JAPAN

The magnetic flux quantum (fluxon) penetrating through a superconducting lead film was observed directly and individually as magnetic lines of force by electron holography based on the Aharonov-Bohm effect[1]. The phase contours of the electron wave not only confirm the quantized flux value h/2e, but also reveal the inner structure of a single fluxon by digital phase analysis technique[2].

With the film thickness < 0.5μm, each fluxon, after penetrating through the film, fans out into the vacuum. We also observed fluxon-antifluxon pairs which play main role in the Kosterlitz-Thouless theory for two-dimensional superconductivity such as high-Tc superconductors. With thicker films, magnetic flux forms a bundle with several multiples of h/2e.

Direct observations of static structures and dynamic behaviors of fluxons by electron holography are expected not only to unveil the mechanism of high Tc superconductivity, but also to promote its industrial application.

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SURVEY OF SUPERCONDUCTIVITY IN A LAYERED COMPOUND 1T-VSe_2

K. Tsutsumi, Y. Ishihara and H. Suzuki*
Department of Physics, Kanazawa University, Kanazawa, Japan
*Department of Physics, Tohoku University, Sendai, Japan

The layered transition-metal dichalcogenides MX_2 (M=V,Nb,Ta; X=S,Se,Te) undergo the charge-density-wave (CDW) phase transition at low temperature. Furthermore, MX_2 exhibits superconductivity at lower temperature. When the CDW transition temperature T_{CDW} is higher, the onset temperature T_S of superconductivity is lower. For example, T_{CDW} is 33.5 K and T_S is 7.2 K for 2H-$NbSe_2$. For 2H-TaS_2 T_{CDW} is 75 K and T_S is 0.8 K.

1T-VSe_2 undergoes the CDW phase transition at 108 K. Therefore, we expect a very low superconductivity transition temperature. We have performed the electrical resistivity measurement in the temperature range from 1.5 K down to 10 mK. We observed a faint decrease from 65 mK down to 10 mK. It might be due to superconductivity. In addition, a slight increase of the resistivity in the temperature range from 1.5 K down to 65 mK is also reported.

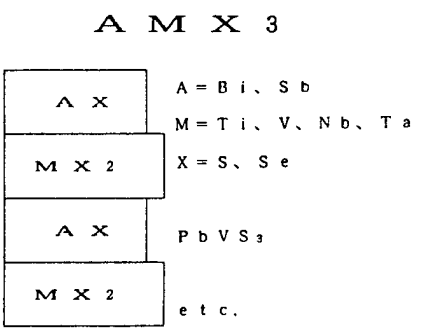
COMPOSITE-LAYERED CHALCOGENIDES: A NEW CANDIDATE FOR SUPERCONDUCTOR

Yoshinao OOSAWA, Yoshito GOTOH, and Mitsuko ONODA*

National Chemical Laboratory for Industry, Higashi, Tsukuba, Ibaraki 305 JAPAN
*National Institute for Research in Inorganic Materials, Namiki, Tsukuba, Ibaraki 305 JAPAN

New type of chalcogenides called "composite-layered chalcogenide" schematically shown in the figure have been prepared for the first time and characterized using electron diffraction, X-ray powder diffraction, preliminary single crystal structure determination, and electric resistivity measurements. The structure of the chalcogenides consists of two-atom-thick layer of AX and three-atom-thick sandwich of MX_2 alternately stacked.

They were prepared as follows Starting materials were mixed together and sealed in a silica tube in vacuum. The tube was placed in an electric furnace, heated at 500 °C, then at 800°C, and cooled to room temperature. The products were obtained as black-grayish microcrystalline powder with luster.



Their electric resistivity measured with DC four-probe method in the range of 1.7 K-300 K showed various behaviors: semiconducting, metallic, or superconducting depending on their compositions and structures.

ANOMALOUS TRANSPORT PROPERTIES OF ORGANIC SUPERCONDUCTOR κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

Hatsumi Mori, Koichi Nakao, Izumi Hirabayashi, Shoji Tanaka
ISTEC 1-10-13 Koto-ku Tokyo 135, Japan
Kokichi Oshima
Okayama University, 1-1-1 Tsushimanaka Okayama 700, Japan

Usually low-purified or poor-crystalized organic conductor does not give a superconducting transition, so that T_c is not varied.

However, κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ with the highest T_c among organic superconductors ($T_c \sim 11K$) affords a variety of T_c and transition behavior, which depends upon purification and preparation conditions. The origin of anomalous transport properties is discussed on the measurement of magnetoresistance and x-ray diffraction.

CONDUCTIVE LANGMUIR-BLODGETT FILMS OF TRIDECYLMETHLAMMONIUM-Au(DMIT)$_2$ AND RELATED COMPOUNDS

T. Nakamura, Y. Miura, M. Matsumoto, H. Tachibana, M. Tanaka,
and Y. Kawabata
National Chemical Laboratory for Industry,
Higashi, Tsukuba, Ibaraki 305, JAPAN.

In this paper, we describe a newly developed conductive Langmuir-Blodgett (LB) film using transition metal complexes. Conductive LB films reported so far are classified as one-dimensional organic conductors, which are very sensitive to the defects in the conduction stacks and have intrinsic instability as one-dimensional system. By the introduction of higher dimensionality, this instability can be suppressed and higher conductivities will be realized. The alkylammonium-metal(dmit)$_2$ complexes are one of the promising candidates for this purpose. This sulfur-rich 1,2-dithiolene complex has provided three kinds of molecular superconductor, TTF[Ni(dmit)$_2$]$_2$, TTF[Pd(dmit)$_2$]$_2$ and Me_4N[Ni(dmit)$_2$]$_2$. By the introduction of alkylammonium group as a counter cation, the complexes become amphiphilic and suitable for the construction of LB film.

Fairly high conductivity was obtained by the use of tridecylmethylammonium-Au(dmit)$_2$. The bulk conductivities of the films at room temperature were ca. 15 S/cm after bromine oxidation and ca. 30 S/cm after electrooxidation. The temperature dependence of electrical conductivity of the latter film measured by dc 4-probe method showed the metallic behavior down to 200 K with weak temperature dependence. Below 200 K, the curve follows Arrhenius equation with the activation energy of 0.002 eV in the range of 200 - 50 K. The value is smaller than those of the LB films reported so far by about one to two order of magnitude. There is distinct deviation from Arrenius plot below 50 K which can be explained by VRH. The film still exhibits the conductivity of ca. 10 S/cm at 10 K. This system will afford promising candidate for the development of superconducting LB film.

INTERGRANULAR FLUX CREEP IN CERAMIC $YBa_2Cu_3O_x$

N.Nakamura, M.Ishida and M.Shimotomai
New Materials Research Center, High Technology Research Laboratories,
Kawasaki Steel Corporation, 1 Kawasaki-cho, Chiba 260, Japan

Temporal decay of the diamagnetic magnetization in ceramic $YBa_2Cu_3O_x$ was measured over a temperature range from 4.2 K to 77 K after zero-field cooling in order to investigate kinetics of magnetic flux penetration into intergranular region. Sintered samples of density up to 95% of theoretical value were prepared by a spray-drying technique. Decay rate of the diamagnetic magnetization under a magnetic field of 30 Oe at 77 K was strongly dependent on the density of samples; the decay rate in a sample of 95%-density was negligibly small while that of a sample of 85%-density was large and its diamagnetization decreased to 91% of the initial value in the first 500 seconds. Temperature dependences of the decay rate were interpreted with a model of thermally activated flux creep at intergranular region. The relevant activation energy was evaluated as 3 meV.

MAGNETIC PROPERTIES OF Bi- AND Tl-BASED SINGLE CRYSTALS

T.Kotani, K.Ohkura, H.Takei and K.Tada
Basic High-Technology Laboratories,
Sumitomo Electric Industries, LTD.,
1-3, Shimaya 1-chome, Konohanaku, Osaka, 554, Japan

Crystal growth and magnetic relaxation of $Tl_2Ba_2Ca_2Cu_3O_x$ and $Bi_2Sr_2CaCu_2O_x$ single crystals were investigated. According to the study on the phase relations of the Bi-Sr-Ca-Cu-O system, large Bi-based single crystals (dimensions : 4mm x 12mm x 2mm) and Tl-based single crystals (dimensions: 1mm x 1mm x 0.2mm) were grown by self-flux method. These crystals were characterized by means of X-ray diffraction measurements and energy dispersive X-ray microanalyses. The superconducting onset transition temperature for Bi- and Tl-based crystals were 88K and 116K, respectively. Magnetization and flux creep of the single crystals were measured with a DC SQUID magnetometer. The field H=0.1T, parallel to c-axis of crystal, was applied after cooling the crystal in zero field. Thereafter, the applied field was returned to zero and the time dependence of magnetization was measured. The single crystal showed a large magnetic relaxation, which was approximately linear with the logarithm of the time. The relaxation rates roughly tend to increase with increasing temperature. Based on the thermal activated flux creep model, the effective flux-pinning potential energy for Bi-based crystal was estimated to be about a hundred meV from these magnetization measurements. The flux-pinning potential energy of Tl-based crystal is roughly twice as large as that of Bi-based crystal. Detailed results of the measurements will be reported.

DISTRIBUTION OF FLUX PINNING ENERGIES IN SUPERCONDUCTING THIN FILMS

Hiroaki Furukawa, Kenichi Kawaguchi and Masao Nakao

SANYO Tsukuba Research Center, Koyadai 2-1, Tsukuba, Ibaraki 305, Japan

We report direct observation of the flux pinning behavior of Tl-Ca-Ba-Cu-O highly oriented thin films and randomly oriented polycrystalline thin films. The phases investigated were $Tl_1Ca_2Ba_2Cu_3O_9$ with zero resistance at 110 K and $Tl_2Ca_1Ba_2Cu_2O_8$ with zero resistance at 90 K. From the temperature dependence of the critical current densities J_c at zero field, activation energies U_0 are estimated to be around 110 meV in common. This shows that U_0 has little dependence on the grain orientation and the kind of crystal phases.

Time-logarithmic magnetic relaxation $M(t,T)$ was observed as well as in a single crystal. Within a thermally activated flux motion (TAFM) model, the distribution of activation energies $\rho(U_0)$ is determined from data on the time and temperature dependence of $M(t,T)$ for the thin films. The presence of a high-energy tail in the distribution suggests that the TAFM model can not be described by a single activation energy U_0; the effective U_0 value increases rapidly with temperature. This fact might be related to a distribution of extended defects in the interior of grains. Experiments for other phases and other superconductors are in progress.

RELAXATION IN HIGH TRANSPORT CURRENT Bi-Sr-Ca-Cu-O SYSTEM

Hironori Matsuba, Akihito Yahara and Kumiko Imai
Yokohama R&D Laboratories, The Furukawa Electric Co.,Ltd.
2-4-3, Okano, Nishi-Ku, Yokohama, 220, Japan

Much research on high temperature oxide superconductors has revealed that thermally activated flux creep controls the dissipation behavior of the superconductors. Persistent current measurements have been reported with toroids of the Y-Ba-Cu-O system and of the Tl-Ca-Ba-Cu-O system. The relaxation behavior of the persistent currents is explained by the spin-glass-like state or by the flux creep theory developed by Anderson.

In a bismuth oxide system, the authors have studied the low Tc phase with a transition temperature of 75-85K to improve both the critical transport current and the critical temperature. We have achieved a superconducting transport current greater than 1000 A/cm^2 at 77K, and zero resistance at temperature exceeding 95K with a $Bi_2Sr_2Ca_1Cu_2O_{8+x}$ composition.

In this report, we shall present a persistent current experiment using a toroid made of the bismuth compound with a critical temperature of 95K. The relaxation behavior is well explained by a simple equation deduced from a power-law characteristic of the I-V property of the superconductor.

RESISTIVE BEHAVIOR OF HIGH Tc SUPERCONDUCTING THIN FILM IN MAGNETIC FIELD

T. Matsuura, S. Tanaka, H. Itozaki and S. Yazu

Itami Research Laboratories, Sumitomo Electric Ind., Ltd.

1-1 Koyakita 1-Chome, Itami, Hyogo,664, Japan

We have calculated a pinning potential energy of epitaxially grown YBCO thin films by measuring the resistance in a magnetic field up to 8T.

Thin films were prepared by an RF sputtering and the film thickness was 600nm. The temperature dependence of resistance in a magnetic field was measured with a dc current density of 40A/cm2. The current flowed in ab planes. An magnetic field were parallel and perpendicular to the ab planes. We have plotted data as log R vs 1/T. These plots have a straight line portion which indicates that the resistive behavior can be explained by a thermally activated flux creep. This slope gives the pinning potential energy(U).

The U had strong anisotropy. U in a parallel field was larger than that in a perpendicular field. The U decreased from 3.5eV to 1.4eV in the parallel field with the increase of the magnetic field from 0.3T to 8T. In the case of the perpendicular field, the U decreased from 1.5eV to 0.4eV. These kind of anisotropy and field dependence are similar to those of YBCO single crystal reported by Palstra etal.

INTERGRANULAR VORTEX AND WEAK-LINK STRUCTURE IN THE Ca AND Ag DOPED $LnBa_2Cu_3O_{7-y}$

FUMIO MIZUNO, HIROMU MASUDA, IZUMI HIRABAYASHI, AND SHOJI TANAKA
SUPERCONDUCTIVITY RESEARCH LABORATORY, NAGOYA DIVISION, ISTEC,
NAGOYA, JAPAN

It is appropriate to describe bulk oxide superconductor as granular materials composed of agglomerates of anisotropic grains separated by grainboundary. The granularity strongly affects the transport critical current density. The low transport critical current density is thought to be related to the weak-link behavior between superconducting grains.

In order to understand the weak-link properties, the behavior of the low-field magnetization hysteresis (0-10 mT) was investigated. Intergranular critical current density estimated from the hysteresis curve is discussed with the effect of intergranular (Josephson) vortex pinning. The temperature dependence of intergranular critical current density in the low temperature region (< 20 K) is interpreted with the thermally activated flux creep model. The systematic investigation on the hysteresis of the transport critical current density will be also discussed as compared with that of the magnetization.

CRITICAL FIELDS, CRITICAL CURRENTS AND FLUX CREEP IN UNTWINNED $TmBa_2Cu_3O_X$ SYNGLE CRYSTALS

V.V.Moshchalkov, A.A.Zhukov, A.A.Gippius, O.V.Petrenko, V.I.Voronkova and V.K.Yanovskii
Laboratory of High T_c Superconductivity, Physics Department, Moscow State University, Moscow 117234, USSR

The first critical fields of the untwinned $TmBa_2Cu_3O_X$ superconducting single crystals were measured along a, b and c-axes. The $H_{C1}(0)$ values are larger than those reported previously for polydomain crystals. Our data determine in the logarithmic approximation the ratio of the penetration depths: $\lambda_a:\lambda_b:\lambda_c=1.7:1.0:4.4$. For H//c the H_{c1} vs T is a linear function for T>10 K. Angular dependences of the Meissner magnetic susceptibility and H_{C1} in the bc-plane were studied. Critical currents $j_c(T)$ in single crystals of different types, including untwinned crystals, were also measured. The $j_c(T)$ curves follow the exponential dependence $j_c(T)=j_c(0)\exp(-T/T_o)$ with $j_c(0)=(2-3)10^6$ A/cm^2. The $j_c(0)$ independence on the density of the domain walls suggests a weak pinning by a twinning plane. Data on the remanent magnetization relaxation RM(t) in untwinned crystals are reported. The rate r(T)=dRM/dlnt has a sharp maximum at $T=T_{max}$ which is shifted to higher temperatures as H is increased. The r(T) kink at T_{max} is caused by a topological transition in the distribution of the Abrikosov vortices and is qualitatively reproduced by the calculation taking into account the thermally activated flux creep and vortices distribution according to the Bean's model.

ENLARGEMENT OF FLUX PINNING FORCES IN X-RAY IRRADIATED $Gd_1Ba_2Cu_3O_{7-x}$ SUPERCONDUCTING THIN FILMS

S.KOHIKI, S.HATTA, K.SETSUNE, K.WASA, Y. HIGASHI,* S.FUKUSHIMA* and Y.GOHSHI
Central Research Laboratories, Matshushita Electric Ind. Co. Ltd., Moriguchi, Osaka 570, Japan, *Faculty of Engineering, University of Tokyo, Hongo7-3-1, Bunkyoku, Tokyo 113, Japan

We have sucessfully introduced stable pinning centers into $Gd_1Ba_2Cu_3O_{7-x}$ superconducting thin films by x-ray irradiation of the sputter deposited film before the annealing in oxygen. The films without x-ray irradiation showed the logarithmic time dependence of remanence as reported before. The activation energy in a flux creep model increased from 0.2eV to 0.7eV due to the x-ray irradiation. The apparent change in x-ray diffraction pattern due to the x-ray irradiation was not observed but the resistivity decreased and T_c increased with the x-ray irradiation.

The films were prepared by rf magnetron sputtering. X-ray irradiation of the as-deposited films was carried out by using an Rh x-ray tube operated at 50kV and 50mA in a vacuum of 10^{-3} Torr for 100 h. Both films x-ray irradiated and unirradiated were annealed simultaneously at 900°C for 2 h and then at 450°C for 2 h in flowing oxygen. The time dependence of the remanence was measured at constant temperature by a SQUID susceptometer. The external field (H_{ex}) was applied parallel to the c axis of the film. The measurement of relaxation started just after H_{ex} returned back to zero.

We speculate that the oxygen defects produced by x-ray irradiation enlarged the flux pinning forces of the crystal.

PROPERTIES OF Bi-Pb-Sr-Ca-Cu-O BULK SUPERCONDUCTORS PREPARED BY A HOT-PRESS METHOD

R.Yoshizaki, H.Ikeda, K.Yoshikawa* and N.Tomita#
University of Tsukuba, Tsukuba, Japan; *Takasago Research and Development Center, Mitsubishi Heavy Industries, Ltd., Takasago,,Japan; #Kobe Shipyard and Machinery Works, Mitsubishi Heavy Industries, Ltd., Kobe, Japan

Pb-doped Bi-Sr-Ca-Cu-O samples with a single high-Tc phase were prepared by a hot-press method, in which a sample was sintered with applying uniaxial pressure of about 300 kg/cm^2 at 822 ^{o}C. Their properties were measured and compared with those for the sample without hot-press (NP) or for the one with intermediate pressing at room temperature (IP). The hot-press (HP) sample shows highly oriented layer structure with maintaining the grain size of NP, while the grains were crashed to small ones for IP samples. The densities measured by a Berman balance method are equivalent to the ideal value of 6.5 for the HP sample, while 6.2 for IP and 6.0 for NP samples, respectively. Magnetization measurement by a SQUID magnetometer shows 100 % shielding effect for HP and IP samples in zero-field cooling process. Meissner effect measured in field cooling process is the smallest for the HP sample, which suggests the large pinning effect for the sample.

Critical current density, Jc, was measured by resistive transition technique. The maximum Jc of 6,250 A/cm^2 was obtained for IP sample at 77.3 K under 0 T. The Jc of the HP sample was not measured precisely, only 4,800 A/cm^2, due to burning out of electrodes. The Jc under magnetic field has been observed in the two configurations, transverse (J⊥B) and longitudinal (J//B); Jc of 1,700 A/cm^2 was obtained for IP at 0.1 T for J⊥B. The Jc has also estimated from the hysteresis of a magnetization curve, and the largest hysteresis was obtained for the HP sample.

NOVEL MAGNETIC TRANSITION IN X RAY IRRADIATED GdBaCuO FILMS

S. HATTA, S. KOHIKI, K. SETSUNE and K. WASA

Central Research Laboratories, Matsushita Electric Industrial Co. Ltd., Moriguchi, Osaka 570, JAPAN

We report a new magnetic transition of GdBaCuO thin films annealed in oxygen after x ray irradiation. The specimen films were irradiated by using x ray tube operated 50kV and 50 mA in 10^{-3} Torr for 100 h with the postannealing at 900°C for 2h and then at 450°C for 2h in flowing oxygen. When H_{ex} was applied perpendicular to the film plane, the large diamagnetization(M = about -10^{4} emu/cc) was suddenly changed to the very small value around H_{ex}=100 Oe at 4.2K, similar to the type 1 superconductor. Once it changed to the small value state, it never recovered to the original state, even if H_{ex} was decreased or temperature was changed. Such an irreversible transition was thought to be the change from the shielding state to the Meissner state. Namely, the fluxoids might suddenly invade into the specimen, different from the case of the specimen without any irradiation treatment. The transition field was not perfectly definite with some distribution, but it was increased in a higher temperature range. This effect might be due to the redistribution of pinning forces, produced by the oxygen defects with the irradiation.

MAGNETIC SHIELD OF HIGH-Tc OXIDE SUPERCONDUCTORS AT 77K IN A WEAK MAGNETIC FIELD

Tomonobu Nakayama, Hiroshi Ohta†, Hitoshi Takayama, Koji Shigematsu, Kazutomo Hoshino, Eiichi Sudoh††, Kazuhiko Katoh, Shigeru Yamazaki, Hidefusa Takahara and Masakazu Aono†

Core Technology Laboratory, Mitsui Mining & Smelting Co., Ltd., Ageo, Saitama 362, Japan
†RIKEN (The Institute of Physical and Chemical Research), Wako, Saitama 351, Japan
††Research & Development Laboratory, Tokyo Super Refractories Co., Ltd., Asamuta, Ohmuta, Fukuoka 836, Japan

Magnetic shielding effects of superconducting Y-Ba-Cu-O and Bi-Pb-Sr-Ca-Cu-O vessels have been studied. Magnetic fields inside a vessel in a superconducting state at 77K were compared with those in a normal state at room temperature by measuring induced voltages in a pick-up coil inside the vessel. Since the induced voltages had been extremely small ($10^{-6} \sim 10^{-10}$ volts) in a superconducting vessel at 77K, we have introduced the Cooled FET Amplifier which works at 77K and amplifies the small signals effectively. In case of Bi-Pb-Sr-Ca-Cu-O vessels, the ratios of the magnetic field at 77K to that at room temperature were $2 \sim 5 \times 10^{-6}$ when magnetic fields of $3 \times 10^{-2} \sim 1$ gauss at a frequency rage of 10 ~ 1000Hz. Both Y-Ba-Cu-O and Bi-Pb-Sr-Ca-Cu-O vessels have the attenuation ratio enough for neuromagnetic measurement with a SQUID magnetometer.

EVALUATION OF MAGNETIC HYSTERESIS CURVES FOR VARIOUS SPECIMENS

Y. Ishikawa, M. Kojima, S. Yoshizawa
Central Reseach Laboratory , Dowa Mining Co., Ltd.,
Tobuki, Hachioji, Tokyo, 192 Japan

Hysteresis curves of various specimens were measured using vibrating sample magnetometer (VSM) to estimate the magnetic charactors. Used specimens are powders of different particle size and bulks made from those powders. The difference of initial magnetization curves and hysteresis curves between powders and bulks were studied.

In case of bulks initial magnetization curve has a shoulder below Hc1, irrespective of no shoulder for powders. This shoulder comes from breaking of the weaklinks between grains.

Value of Hc1 increased as the particle size of powders decreased from 50 um to 1 um. Volume fraction of supercoducting phase for powders was relatively proportional to the particle size.

By increase of scanning rate of magnetic field, hysteresis loop widened. This result indicates that current induced from the change of magnetic field increases the magnetization.

CRITICAL CURRENT DENSITY MEASUREMENTS BY OPPOSITELY POLARIZED MAGNETIC DIPOLES

Kouichi Shintomi, Hironori Matsuba
Yokohama R&D Laboratories, The Furukawa Electric Co.,Ltd
2-4-3, Okano, Nishi-ku, Yokohama, 220, Japan

Critical current density is one of the most important measures of superconductors. A four-probe measurement or an estimation from magnetic hysteresis are usually carried out to acquire the critical current density, however, the difficulty sometimes comes in determining critical current density of large superconductor.

We have developed a new method to estimate critical current density. Two oppositely polarized magnetic dipoles formed by current loops of small coils are arranged against superconductor and magnetic field are produced in a small area along the surface of the superconductor.
The magnetic field strength onto the surface depended on the penetration of the magnetic flux into the superconductor.
The critical current density of the small area of the superconductor is estimated from the field dependence.

This paper describes the principle of determining critical current density of a superconductor, positional scatter of a superconductor in critical current density and the magnetic property.

NONRESONANT MICROWAVE ABSORPTION AND CRITICAL CURRENT DENSITY IN HIGH T_c SUPERCONDUCTORS

Akiharu MORIMOTO, Minoru MAKIDA, Akihiro MOTO and Tatsuo SHIMIZU
Department of Electronics, Faculty of Technology,
Kanazawa University, Kanazawa 920, Japan

In order to increase the macroscopic critical current density J_c in high T_c superconductors, it is important to reduce the weak links between grains and to introduce the pinning centers in grains. Superconducting properties in grains is mainly characterized by the microscopic J_c. Therefore it is important to estimate each of J_c separately in order to increase the macroscopic J_c.

In this study, the transport critical current measurement with four probe method was performed at 77K for bulk samples in order to obtain the macroscopic J_c, and the nonresonant microwave absorption (NRMA) measurement instead of the magnetization measurement was performed at 77K for powdered samples with a submicron size in order to characterize the superconducting properties within grains. The amount of nonsuperconducting impurity phase, which appears to contribute both to the weak links and the pinning centers, was estimated by ESR measurement at room temperature. Ba-Y-Cu-O and Bi-Sr-Ca-Cu-O samples were prepared by the conventional sintering method in dry oxygen with various sintering temperatures.

As a result, it was found that the samples with the largest macroscopic J_c around $200A/cm^2$ also show the largest NRMA intensity but the amount of the impurity phase in those samples is not a smallest one. The former finding suggests that the macroscopic J_c in this level is affected not only by the intergrain properties but also by the intragrain properties. Furthermore it was found that there is a difference in the hysteresis of magnetic-field dependent NRMA between Ba-Y-Cu-O and Bi-Sr-Ca-Cu-O, suggesting a difference in the pinning characteristics between them.

MAGNETIZATION HYSTERESIS IN THE BiPbSrCaCuO SUPERCONDUCTING SYSTEM

M. Green, K. Nakatani, T. Hasegawa, K. Kishio, K. Kitazawa
University of Tokyo, Tokyo, Japan

Magnetization hysteresis of BiPbSrCaCuO samples, both polycrystalline and single crystalline, was measured. Vibrating sample magnetometry was used to obtain high field (up to 9 T) magnetization curves as a function of temperature down to 4.2 K. In general, the magnetization and its hysteresis were found to be strongly dependent on temperature, decreasing rapidly at higher temperatures. The phase distribution of the polycrystalline samples, triple-layer (110 K) phase, double-layer (80 K) phase, or a mixture of these phases, was found to have a strong effect on the magnitude of the irreversibility (ΔM) as well as its dependence on temperature. Emphasis in this study is placed on possible correlations between microstructural characteristics and macroscopic magnetic properties. Effects of heat treatment conditions and addition of various foreign elements will be reported. Foreign element addition was studied in an effort to produce small precipitates that could possibly affect flux pinning characteristics and thereby critical current density; our results will be interpreted in this context.

A.C. SUSCEPTIBILITY OF YBaCuO PREPARED BY QUENCH AND MELT GROWTH PROCESS

S.Gotoh, M.Murakami, H.Fujimoto, and N.Koshizuka

Superconductivity Research Laboratory,
International Superconductivity Technology Center,
1-10-13, Shinonome, Koto-ku, Tokyo 135 Japan

A.C. susceptibility measurements have been carried out on YBaCuO prepared by the quench and melt growth process. The temperature dependence of the real component X', and the imaginary component X", of the susceptibility dose not indicate the presence of weak-link regions in the sample. The superconducting transition width of X' is very narrow and only a single peak of X" is observed as differed from bulk sintered materials prepared by the powder mixture method. This substantiates their D.C. magnetization behaviour that can be well explained by the critical state model. The observed relationship between X' and X" shows the validity of the Bean's critical state model .

We also compare the A.C. susceptibility of YBaCuO fabricated by different melt processes and powder mixture method.

CRITICAL CURRENT DENSITY IN $Y_1Ba_2Cu_3O_{7-X}$ EVALUATED WITH PULSED MAGNETIC FIELD METHOD

Shun-ichiro Tanaka and Takayuki Naba

New Materials Engineering Lab., Toshiba Corporation
2-4, Suehiro-cho, Tsurumi-ku, Yokohama, 230 Japan

Critical current density (Jc) in $Y_1Ba_2Cu_3O_{7-X}$ wax evaluated with a derivative of current change induced by pulsed magnetic field. This method enables to eliminate the effects of ohmic contact at potential leads. When a magnetic field is applied to a superconductor ring, two types of current are induced in it to cancel applied field : one is a transport current along the ring and another is a locallized shielding current in a grain. The former coincides with that measured with 4 potential leads and the latter with magnetization curve. Since current direction picked up by a pair of search coil is different with each other, these currents can be measured separately at each temperature from a zero point of the induced current derivative.

Jc of transport current in $Y_1Ba_2Cu_3O_{7-X}$ prepared by pressureless sintering were 500A/cm^2 at 77K, 1250A/cm^2 at 50K and 1500A/cm^2 at 40K, whereas that of locallized shielding current was the order of 10^5A/cm^2. The difference between them might be attributed to weak links at grain boundary. The effects of hot pressing and moisture deterioration were also monitored and discussed. As the derivative curve contains information on flux creep and flux flow in the normalstate, these characteristics were also discussed.

IS OXYGEN DEFICIENCY AT GRAIN BOUNDARIES THE ORIGIN OF WEAK LINKS IN $YBa_2Cu_3O_y$ SINTERED MATERIALS ?

K.Egawa, T.Umemura, M.Wakata, and K.Yoshizaki
Mitsubishi Electric Corp., Materials & Electronic Devices Lab.
1-1-57 Miyashimo Sagamihara-shi, Kanagawa 229, Japan

IS OXYGEN DEFICIENCY AT GRAIN BOUNDARIES THE ORIGIN OF WEAK LINKS IN $YBa_2Cu_3O_y$ SINTERED MATERIALS ?

K.Egawa, T.Umemura, M.Wakata, and K.Yoshizaki
Mitsubishi Electric Corp., Materials & Electronic Devices Lab.
1-1-57 Miyashimo, Sagamihara, Kanagawa 229, Japan

The relationship between the oxygen deficiency and the weak links in sintered $YBa_2Cu_3O_y$ has been examined by transport current and magnetization measurements for quenched samples, dropped into a vessel filled with liq. N_2 at various temperatures. For the furnace cooled sample (a) and the sample (b) quenched at 500°C , the following results are obtained : (1) It is seems that the sample (a) and (b) are single-phase of $YBa_2Cu_3O_y$ by X-ray diffraction measurements. The oxygen content for the sample (b) is less by 0.28wt% ($\Delta y=0.14$) than that for the sample (a). (2) The $T_{c(\rho=0)}$'s for the sample (a) and (b) are 90 and 89K, respectively. (3) The transport critical current densities at 77K,0T are 190 and 59A/cm^2, respectively. The field dependence of the J_c for the sample (b) is much stronger than that for the sample (a). (4) The intra-grain J_c-B characteristics, calculated from the hysterisis of the magnetization, are almost the same. These results suggest that the oxygen deficiency at grain boundaries is the origin of the weak links in $YBa_2Cu_3O_y$ sintered materials.

HIGH-Tc SUPERCONDUCTING Bi-Pb-Sr-Ca-Cu-O AND Tl-Ba-Ca-Cu-O FILAMENTS PRODUCED BY THE SUSPENSION SPINNING METHOD

Tomoko Goto and Tamotsu Maruyama
Nagoya Institute of Technology,
Nagoya, Japan

High-Tc superconducting Bi-Pb-Sr-Ca-Cu-O and Tl-Ba-Ca-Cu-O filaments were successfully prepared using a combined technique of suspension spinning and densification of the pyrolyzed filaments by pressing and sintering. The Jc of the filament was affected by the spinning and sintering conditions.

Although the starting Bi system oxide with a single high-Tc phase was used, the proportion of the high-Tc phase in the filament obtained was dependent on the pyrolyzed conditions. Zero electrical resistivity state (Tc) was achieved at 100 K and the maxium Jc observed so far was 1500 A/cm² at 77 K for the filament densified by two stage of pressing and sintering at 1113 K for total time of 30 h in low O_2 of 1/13 atom after pyrolyzed at 773 K for 1800 s. The filament consisted of a single high-Tc phase and the grains were oriented with the c-axis perpendicular to the longitudinal direction of the filament. The filament exhibited a tensile strength of 55 MPa and an elongation of 1.1 %.

The Tc of the Tl-Ba-Ca-Cu-O (A) and Tl-Ba-Sr-Ca-Cu-O (B) superconducting filaments increased with increasing the sintering temperature ranging from 1133 K to 1183 K. The (A) and (B) filaments which were pressed and sintered at 1183 K for 600 s after pyrolyzed at 773 K for 1800 s, have high Tc such as 98 and 100 K and high Jc values of 1045 A/cm² and 980 A/cm², respectively. The densification process was repeated, however, the enhancement of Jc was not detected. The (A) filament consisted of a single low-Tc phase of 98 K and (B) filament was a mixture of the low-Tc and high-Tc phases. Any prefered orientation of crystals was not detected for these Tl system oxide filaments.

IMPROVEMENT OF GRAIN BOUNDARY WEAK-LINK IN TAPE SHAPED WIRE PREPARED BY DIRECTIONAL MELT-GROWTH TECHNIQUE.

M.OKADA, R.NISHIWAKI, T.MATSUMOTO, T.KAMO, K.AIHARA, and S.MATSUDA., Hitachi Research Laboratory of Hitachi, Ltd., Hitachi*Ibaraki 319-12 JAPAN.; M.SEIDO, Metal Research Laboratory of Hitachi Cable Ltd., Tsuchiura, Ibaraki 300, JAPAN.

Improvements in microstructure, designed to enhance the critical current density (Jc) of HTSC superconducting wire in an applied magnetic field, is a matter of some urgency. In this study, dense and aligned high-Tc superconductor tapes with metallic sheath were prepared by the directional melt-growth technique, called 2D-TSZM(Two-Dimensional Traveling Solvent Zone Melting). The 2D-TSZM was successfully realized to improve the grain boundary weak-link behavior in HTSC superconducting tape. The Jc of the tape reached 1,000 A/cm^2 at 77K in 1T. It was observed that the plate shaped Y-123 or Tl-2223 crystals (1 to 10 mm long and 0.1mm thick) including fine second phases (ex. Y-211 crystals) were alignedparalleito the longitudinal direction of the tape. Jc's and flux pinning characteristics of several tapes will be discussed in relation to each individual microstructure.

FERMION CONFINEMENT MODEL FOR HIGH-T_c SUPERCONDUCTIVITY IN A QUASI-TWO-DIMENSIONAL SYSTEM

[1]K. FUKUSHIMA and [2]H. SATO
[1]Toshiba Research and Development Center, 4-1, Ukishima-cho, Kawasaki-ku, Kawasaki 210, Japan
[2]Department of Physics, Hyogo University of Education, Yashiro-cho, Kato-gun, Hyogo 673-14, Japan

In spite of many theoretical attempts to explain the high-T_c superconductivity of copper oxides, the dominant mechanism has not yet been identified. Experiments show that carrier holes are Fermi-liquid-like in the normal state and form s-symmetry pairing in the superconducting state. Copper oxides have layered structure with two-dimensional (2D) electron systems. It has been observed that T_c decreases below 5 K when electron systems become 3D. We study the 2D effect on the superconducting pairing interaction via longitudinal optical (LO) phonons of long wavelength. We treat a quasi-2D system where electrons are confined within a 2D x-y plane and they interact with 3D phonons. It is shown that the exchanged phonon momentum in the electron-electron scattering is oriented in the x-y directions because of the momentum conservation law. The electric field produced by LO phonons is then squeezed within the x-y directions. The effective electron-electron interaction potential in this case becomes logarithmic, which is quite different from the one widely used. This 2D effect is known as the fermion confinement in the field theory. The logarithmic potential raises the superconducting T_c up to about 100 K. The isotope effect in our context becomes small, since the Coulomb pseudo-potential is about half of the electron-phonon interaction strength. Thus, the high-T_c is explained by the BCS theory with our 2D effective potential.

Reference: K. Fukushima and H. Sato, physica status solidi (b) 153, K141 (1989).

GROUND STATE ELECTRONIC STRUCTURE AND MECHANISM OF HIGH-T_C COPPER OXIDES

Yoshihiro Asai, Electrotechnical Laboratory, Tsukuba Ibaraki 305 Japan

Ground state electronic structure of high-T_c copper oxides have been determined from quantum chemical calculations of the clusters whose potentials are modified by the Madelung potentials to simulate the bulk effects within the cluster model.[1)]

The electronic correlation in the oxides is taken into account in the calculations. The charge iteration has been performed and we obtained self-consistent result within the model. A separate estimate of the bandwidth is used as a small correction.

Our calculation is unique among the similar calculations in that we estimate the effect of Madelung potential to the electronic structure rigorously and obtained self-consistent charge distribution between the cluster and the surrounding point charges. Possible mechanisms[2)] relevant to this electronic ground state will be discussed.

1) Y.Asai, J.Phys.Soc.Jpn.58(1989) in press.
2) Y.Asai, J.Phys.Soc.Jpn.57,3491(1988).

EFFECT OF COLD-WORKING ON THE CRITICAL CURRENT DENSITY OF Ag-SHEATHED Bi(Pb)-Sr-Ca-Cu-O TAPES

Sang-Soo Oh, Kozo Osamura and Shojiro Ochiai
Department of Metallurgy, Kyoto University,
Sakyo-ku, Kyoto 606, Japan

In order to get a high critical current density in the Ag- sheathed Bi(Pb)-Sr-Ca-Cu-O superconducting tapes, the effect of heat treatment and cold working (swaging, rolling, drawing and pressing) has been investigated in detail. High critical current density could be obtained by a combination of various processes. A most effective one was the repeat of pressing and heat treatment at 1103 K after the reduction by swaging. Also the optimization of the chemical composition was found to be very important for achieving high critical current density. The critical current density increased abruptly with decreasing tape thickness below a critical thickness. From the microstructure observation, the sepcimen with critical current density of 8100 A/cm^2 at 77K consisted of two major phases (so called high Tc and low Tc phases) and three minor ones. The pole figure indicated significantly the (001) preferred oriented sturucture parallel to the tape surface. The improvement of critical current density was attributed to the structural refinements such as textured grain structure, high densification and so on.

NEW FABRICATION METHOD OF THICK FILM OF OXIDE SUPERCONDUCTOR BY THE COMBINATION OF MIST PYROLYSIS AND COLLISION OF PARTICLES TO SUBSTRATE

Masanobu AWANO and Hiroyoshi TAKAGI

Government Industrial Research Institute, Nagoya

1-1 Hirate-cho, Kita-ku, Nagoya 462 JAPAN

New fabrication method of film deposition of oxide superconductor was developed. It is demanded to fabricate superconducting dense film without heat treatment after or through deposition process. We succeeded to fabricate thick film by combining the mist pyrolysis method with the gas phase deposition method. Detail of processing is described below.

An aqueous solution of Y,Ba,and Cu nitrates was prepared, and then atomized by ultrasonic nebulizer. Generated droplets were carried by oxygen gas into reaction zone kept at 950-1000°C and pyrolyzed. They crystallized directly to superconducting phase. Produced superconductive particles with submicron scale were carried to vacuum chamber. And then, they were collided and deposited on substrate through a nozzle.

Thickness and wide of the film were varied by the factor such as supplying rate of droplets, solution concentration, removing speed of substrate, and so on. As-deposited film showed dense structure.

figure: Profile of as-deposited film of oxide superconductor fabricated by the collision of well crystallized particles.

EFFECT OF PARTICLE SIZE ON SINTERING BEHAVIOR OF $Bi_2Sr_2CaCu_2O_{8+\delta}$

H.SAKAI, M.YOSHIDA and H.YOSHIDA

MATERIALS RESEARCH LABORATORY, NGK INSULATORS, LTD.
2-56 Suda-cho, Mizuho-ku, Nagoya 467 JAPAN

The effect of particle size of the rapidly quenched amorphous starting powder on the sintering of $Bi_2Sr_2CaCu_2O_{8+\delta}$ thick film in oxygen atmosphere was studied to clarify the behavior of partial melting, which is a requisite process for Bi-compound superconductors to obtain the high Jc values.

The Jc values depended on the sintering temperature, the keeping time and the particle size of the starting powder. In the case of 30 min sintering (partial melting), the temperature ranged between 890 and 905°C to obtain high Jc. The Jc values dropped abruptly at both more than 905°C and less than 890°C. As the particle size of the starting powder became smaller, the maximum Jc value tended to shift to the shorter keeping time and the lower sintering temperature.

It is suggested that the appropriate melting speed may be controlled by the surface area of the particle as well as the temperature. The possible mechanism that explains the effect of particle size on the partial melting behavior will be discussed.

MECHANICAL PROPERTIES OF HIGH Tc OXIDE COMPOSITE SUPERCONDUCTORS

Kozo Osamura, Shojiro Ochiai, Kenji Hayashi
Department of Metallurgy, Kyoto University,
Sakyo-ku, Kyoto 606, Japan

In the technological view point for manufacturing the long scale magnet wire, the mass productive powder-in-tube process seems to be very effective. However both the critical current densities and mechanical properties reported for the Ag sheathed composites are still fairly far from the practical level. So it is urgently necessary to solve these difficulties. In the present paper, two types of oxides, Y-Ba-Cu-O and Bi(Pb)-Sr-Ca-Cu-O, have been investigated. Silver sheathed composite wire and tape were prepared by a combination of various cold working techniques; swaging, rolling, drawing, and pressing. The specimens were heat-treated at the optimum conditions for obtaining high critical current density. The tensile behaviour and its influence on critical current density have been examined. The oxide core showed generally multiple fracture under applied tensile stress. The heavier the cold working results in the higher critical current density and tensile strength. The repetition of heating and cooling between room temperature and 77 K degenerates seriously both critical current density and the mechanical properties. These phenomena have been analyzed using the model of two-components composite structure. Also the present status of investigations on mechnaical properties of high Tc superconductors has been briefly reviewed.

AC LOSS OF HIGH-TC SUPERCONDUCTOR

S.TANAKA, N.ICHIYANAGI THE FURUKAWA ELECTRIC COMPANY,LTD. CHIBA, JAPAN

K.OKANIWA, T.HARA, T.YAMAMOTO TOKYOU ELECTRIC POWER COMPANY,INC. TOKYO, JAPAN

Since high-Tc superconductors have very small lower-critical fields Hc1, a high-Tc superconducting cable of practical size for power transmission should be so designed that its self-field exceeds Hc1. For this reason, AC loss is greater and its evaluation is of importance. Magnetization curves of Y type and Bi type silver-sheathed wires were measured by the DC and AC magnetization technique. Hysteresis losses were derived from these magnetization curve. The result suggests that the Bean model provides a rough evaluation of hysteresis losses in high-Tc superconducting wires which is supposed to be the main component of AC losses.

AG-DOPED BI-SR-CA-CU-O SUPERCONDUCTOR PREPARED BY FLOATING ZONE METHOD

Kazuo Michishita, Noriyuki Shimizu, Yutaka Higashida, Hisanori Yokoyama, Yumi Hayami, Tsutomu Tsunooka, Eikichi Inukai, Yukio Kubo, Akira Saji*, Noboru Kuroda*, Hiroshi Yoshida*
Japan Fine Ceramics Center,2-4-1 Mutsuno,Atsuta-ku,Nagoya 456
*Chubu Electric Power Co.,Inc.,20-1 Kitasekiyama,Odaka-cho,Midori-ku,Nagoya 459

The authors have been studying the preparation of dense and highly oriented bulk sample of Bi-Sr-Ca-Cu-O superconductor by floating zone (FZ) method. Recently Ag-doped bulk samples were prepared aiming at improvement of weak link between superconducting grains and lowering of contact resistance at current terminal.

Bulk samples with nominal composition of $Bi_2Sr_2CaCu_2O_y$ doped with 0 -20 wt% Ag were prepared in an image furnace at growth rates of 2 - 5 mm/h. It was found that Ag particles tend to form dendrite structure aligning along the growth direction. High Jc value over 5,000 A/cm^2 (77 K, 0 T) was obtained in annealed sample doped with 10 wt% Ag. The improvement of weak link by Ag-doping was not clear. On the other hand, annealing was effective for Jc enhancement probably due to improvement of weak link.

The contact resistance at current terminal was effectively lowered by Ag-doping. In Ag-doped sample, low ohmic contact was realized, whose resistance value was less than 1/500 of that in undoped sample, showing metal-like positive temperature dependence. In undoped sample, Jc values decreased with current pulse width. This result was explained by the temperature rise at current terminal due to high contact resistance. On the contrary, Ag - doped sample showed Jc characteristics independent of pulse width.

FABRICATION AND CRITICAL CURRENT DENSITY OF HIGH-Tc Bi-Pb-Sr-Ca-Cu-O SUPERCONDUCTING THICK FILMS

K. HOSHINO[1], H. TAKAHARA[1] and M. FUKUTOMI[2]
[1]Corporate R & D Center, Mitsui Mining & Smelting Co., Ltd.
1333-2 Haraichi, Ageo-shi, Saitama 362 Japan
[2]National Research Institute for Metals, Tsukuba Laboratories
1-2-1 Sengen, Tsukuba, Ibaraki 305 Japan

High-Tc superconducting Bi-Pb-Sr-Ca-Cu-O thick films have been successfully prepared on Ag tapes by using the combination processes of screen printing, cold rolling and sintering. These tapes with highly c-axis-orientation normal to the Ag substrates show a zero resistance of around 105 K. It is found that the cold rolling process drastically improves the packing density of screen printed films as well as the critical current density Jc of the tape. The screen printing pastes with several different compositions have been prepared. The Jc of the tape is very sensitive to the composition and postprinting annealing temperature of the films. The stoichiometric composition of Sr:Ca:Cu=2:2:3 is essential in obtaining the higher Jc of the tape. A partially melt process improves the c-axis alignment of the grains in the films. For the nominal composition ratio of Bi:Pb:Sr:Ca:Cu=1.8:0.4:2:2:3, the Jc of the film on the Ag tape is as high as 10^4 A/cm^2 at 77 K in a zero magnetic field. The optimization in the composition, thickness and annealing condition of the films is in progress.

BASIC CONCEPT OF SUPERCONDUCTORS TEST ITEMS FOR POWER APPARATUS IN SUPER-GM

Kiyotaka Uyeda, Shinichiro Meguro, Takashi Saitoh, Kenichi Takahashi,
Hideo Hatakeyama, Shunichi Hirose, Masakazu Sunada
Engineering Research Association for Superconductive Generation
Equipment and Materials (Super-GM), Osaka, Japan

In Super-GM, a project for developing superconducting generation system has started since September, 1987, and an important subject in this project is the development of superconductor for electrical power apparatuses, especially rotating machines such as synchronous generators. The superconductor will be used under high magnetic field and high stresses with both centrifugal force and transient electro-magnetic force, and thus, the operational condition is quite different from stationary magnets such as accelerators.

Metal based superconductors have been developed over twenty years, and based on those back-ground, suitable testing methods, measuring equipments and requiring items for evaluating the superconductors have been studied in Super-GM. Test items for oxide based superconductors also have been investigated with reference to those of metal based superconductors. It is necessary to evaluate the possibility of the wire technologies including higher current density, long and uniform fabrication and so on. In this paper, the present situation in Super-GM is described.

FORMATION PROCESS OF THE 2223 PHASE AND VARIATION OF COMPOSITION IN BI(PB)-SR-CA-CU-O SUPERCONDUCTOR

Toranosuke Ashizawa, Shuichiro Shimoda, Minoru Ishihara, Keiji Sumiya, Shozo Yamana and Hideji Kuwajima

Ibaraki Research Laboratory, Hitachi Chemical Co., Ltd.
Katsuta-shi, Japan

Partial substitution of Pb for Bi in the Bi-Sr-Ca-Cu-O system result in the increase of the fraction of the 2223 phase. It is difficult to prepare pure 2223 superconductor because of the existence of intergrowth. In this study, bulk Bi(Pb)-Sr-Ca-Cu-O superconductors were fabricated from solid state raw materials, and the chemical composition was analyzed by EDX and the formation process of the 2223 phase was investigated.

Bi(Pb)-Sr-Ca-Cu-O sintered for 20 hours contain the 2223 phase, the 2212 phase, (Sr,Ca)-Cu-O, and (Sr,Ca)-Pb-O. The sample sintered for 100 hours appears to be almost the 2223 single phase by X-ray diffraction and magnetic susceptibility change, but insulating (Sr,Ca)-Cu-O grains exist with the 2223 phase in this sample. The chemical composition varies along the c-axis of a 2223 grain, but it is constant along the (001) plane. The variation in composition indicates the possibility that several superconductor phases exist in a grain and that substitution of Bi,Sr,Ca, and Cu occurs. It is considered that the 2223 phase could be synthesized by the reaction of the 2212 phase and (Sr,Ca)-Cu-O.

EFFECT OF RARE EARTH SUBSTITUTION ON $REBa_2Cu_3O_X$ SUPERCONDUCTORS BY QUENCH AND MELT GROWTH (QMG) PROCESS

M. Morita, K. Sawano, K. Doi, A. Hayashi, K. Kimura, K. Miyamoto and S. Matsuda
R & D Labs - I, Nippon Steel Corporation
1618 Ida, Nakahara-ku, Kawasaki 211 Japan

Effect of rare earth (RE) substitution on $REBa_2Cu_3O_X$ (123) superconductors was investigated in terms of crystal growth and superconducting properties using the Quench and Melt Growth (QMG) process. Starting materials were melt-quenched 123. Soaking treatments were performed at various temperatures for formation of the 123 after partially melting the sample. The 123 formation temperature (T_f) varied with the RE elements. La-, Nd- and Sm- were found to have higher T_f values, while Yb- and Lu- had lower T_f values than the Y-system. In the Y-system, 123 forms by a peritectic reaction between Y_2BaCuO_5 (211) and liquid. However, since 211 does not exist in such system as Nd- and La-, a different reaction was observed from the Y-system in which the product consists of the 123 grains with fine 211 dispersoids.

Superconducting properties of rare earth substituted QMG materials were similar to those of the Y-system. They exhibited the sharp transition and high critical current densities (J_C). The J_C was affected by their microstructures which indicates why microstructural development is important.

Since the rare earth substitution in the QMG process allows us to increase the controllability of the process variables such as the reaction temperature, it is expected that optimization of the process can be achieved more easily.

THE TRANSPORT PROPERTIES OF OXIDE SUPERCONDUCTORS BY MELT PROCESS.

Hiroyuki Kikuchi, Kaname Matsumoto and Naoki Uno.

The Furukawa Electric Co., Ltd. Yokohama, 220 Japan

The raw materials of YBCO oxide superconductors were mixed and calcined, then pressed and sintered. The oriented $YBa_2Cu_3O_{7-x}$ poly-crystals were fabricated by one directional solidification from molten states of the sintered bulk. In this specimens, the 211 phases were precipitated in the 123 matrix phases, and dispersed several micron meter. We measured transport critical current density (Jc) by micro-four-probe method. The magnetic field dependences of Jc in which field was parallel to the ab plane, were $1x10^5 A/cm^2$ (77K,0T) and $1x10^4 A/cm^2$ (77K,1T). We evaluated dominant pinning sites by Jc-B properties based on the flux pinning theory. According to the result, we presumed that the dominant pinning sites were normal phases in the grains and grain boundaries themselves.

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FABRICATION AND CHARACTERISTICS OF MULTI-CORE Tl-Ba(Sr)-Ca-Cu-O SUPERCONDUCTING TAPES.

M.Seido, F.Hosono, T.Umezawa, A.Nomoto and K.Nomura, Metal Research Laboratory of Hitachi Cable Ltd.; T.Matsumoto, Hitachi Research Laboratory of Hitachi Ltd., Ibaraki, Japan

Superconducting single-core tapes fabricated by SSRP (Silver Sheath & Rolling Process) showed relatively high critical current densities (Jc); 10,300 A/cm^2 in Tl-Ba(Sr)-Ca-Cu O at 77K and 0 T. Multi-core tapes are expected to improve Jc and stability performance, since the excellent characteristics of metallic superconductors are attained in the form of multi-core wire.

In the present study silver sheathed multi-core tapes were fabricated using Tl-Ba(Sr)-Ca-Cu-O and their superconducting charactoristics were investigated in various conditions.

A number of silver sheathed Tl-Ba(Sr) Ca-Cu-O tapes with 36 and 1,332 cores were fabricated in various cross-sectional sizes by SSRP. Jc values of the 36 core tapes increase according to the decrease of the tape thicknesses as same as in the case of single-core tapes. The highest Jc value 5,800 A/cm^2 was attained with the 36 core tape of 0.07 mm thickness. Jc values of the 1,332 core tapes were lower than those of the 36 core tapes in various thicknesses. Observation of cross section revealed a non-uniform area of superconducting filaments.

Bending tests were carried out with the multi core tapes. The 36 and the 1,332 core tapes could endure higher strains than the single-core tapes. Jc values of the 36 and the 1,332 core tapes were constant with the bending strains less than 0.3 and 0.5 %, respectively.

MELT PROCESSING OF YBaCuO OXIDE SUPERCONDUCTORS

H.Fujimoto, M.Murakami, S.Gotoh, N.Koshizuka, T.Oyama and Y.Shiohara

Superconductivity Research Laboratory,
International Superconductivity Technology Center,
1-10-13, Shinonome, Koto-ku, Tokyo 135 Japan

We report various melt processes for YBaCuO superconductors that show high Jc. Microstructural observation has been conducted at each step of fabrication processes using scanning electron microscopy, optical microscopy and transmission electron microscopy. The superconducting phase is produced by the peritectic reaction of the Y_2BaCuO_5 and the liquid. These processes are extended processes of the QMG method proposed by Murakami et al. to produce bulk high Jc superconductors. Strongly aligned structures have been observed, which are promissing for high Jc.

The superconducting properties of YBaCuO fabricated by different melt processes will be compared.

HIGHLY TEXTURED SUPERCONDUCTING Bi-Sr-Ca-Cu-O CRYSTALS PREPARED BY THE VERTICAL BRIDGMAN METHOD

T.Izumi, T.Oyama, and Y.Shiohara
Superconductivity Reseach Laboratory, Tokyo, Japan

The vertical Bridgman method is one of the important unidirectional solidification techniques for making aligned bulk crystals. However, very few successful runs for superconducting oxides by this method have been reported. We investigated the effects of temperature gradient (G) and growth rate (R) on characteristics of unidirectionally grown crystals including texture, mophology, grain size, and phases.

The sample, as an example, grown at the rate of 1 mm/h in a magnesia crusible (5 mm in inner diameter) with nominal composition of $Bi_2Sr_2CaCu_2O_y$ shows a highly textured structure (see in Figure.1).

The values of T_c(onset) and T_c(zero) of this sample were 87K and 68K , respectively. The results of the samples produced in different process conditions will be discussed in detail.

This work has been supported by the R&D Basic Technology for Future Industries through New Energy and Industrial Technology Development Organization (NEDO).

Figure.1 Textured macrostructure of the specimen produced by the Bridgman method

SUPERCONDUCTING HIGH-T_c OXIDE/METAL MATRIX COMPOSITES PRODUCED BY INTERNAL OXIDATION OF UNIDIRECTIONALLY SOLIDIFIED Ag-Yb-Ba-Cu ALLOYS.

Daniel R. Dietderich, Hiroaki Kumakura, and Kazumasa Togano
National Research Institute for Metals, 1-2-1, Sengen, Tsukuba, Ibaraki 305, JAPAN

A superconducting high-T_c oxide/metal matrix composite was produced by internal oxidation of unidirectionally solidified Ag-Yb-Ba-Cu alloys (UDA's). The initial alloys were prepared by arc-melting metallic precursors. The Yb:Ba:Cu ratio of the alloys was fixed at 1:2:3 and the amount of Ag was adjusted to produce alloys with the composition Ag-Xat.%($Yb_1Ba_2Cu_3$), X=18,23, 30. Rods were cut form the ingots and unidirectionally solidified in a vertical tube furnace at 1000°C.

The microstructure of the UDA's is a function of many variables. However, the dominant three are: sample composition, solidification rate, and the temperature gradient at the solid-liquid interface. To reduce the number of variables the temperature gradient was fixed at about 50°C/cm by the furnace geometry and the set temperature. For a solidification rate of 1.5cm/h a eutectic-like lamellar microstructure with lamellae aligned parallel to the solidification direction is produced in an alloy with X=23. The alternating lamellae have two distinct microstructures and compositions. One type of lamella is composed of a single constituent (i.e. it has a uniform in appearance). While, the other type of lamella has four distinct constituents. When the alloy composition deviates from X=23 the lamellar structure is interrupted by Ag-rich (for X=18) and Cu-rich (for X=30) dendrites.

During oxidation of the UDA's the superconducting phase nucleates preferentially in the lamellae with four constituents and at the boundaries between the two types of lamella. The highest overall J_c, and T_c (zero resistance) obtained was 250A/cm^2 and 85K, respectively, for an alloy with X=23. The other alloys which have a different composition and, as a result, a dendritic structure, have lower T_c's and J_c's. This must result form the interruption of the lamellar structure.

A THERMAL GRADIENT TECHNIQUE FOR ACCELERATED TESTING OF Tl-HTSC (or, for that matter, any ceramic!)

P. E. D. Morgan, * M. Okada and T. Matsumoto,
Hitachi Research Laboratory of Hitachi Ltd.,
Hitachi, Ibaraki, 319-12, Japan.

Ceramics are usually formed at high temperature; for success, invariably it is necessary arduously to elucidate the fabrication/temperature response and understand the derivative properties. Increasing ceramic complexity, as with the new HTSC, leads to ever more onerous experiments.

In this new method, a known linear thermal gradient is established, and maintained, for several hours along the ~10 cm length of a silver-sheathed Tl-2223 tape. After sectioning and polishing, the microstructural evolution of the ceramic core, as a function of temperature, is revealed by optical and scanning electron microscopy. Regions of sudden change are identified and associated with eutectic temperature and phase or compositional changes. In one small temperature change regime, more pure 2223 suddenly appears as large lathelike crystals from the less uniform and unreacted matrix. XRD, SEM, electrical and magnetic properties, measured on selected regions, are combined with detailed examination of grain-boundaries (e.g.) and with chemical analysis (EDAX, STEM) allowing accelerated optimization of desired properties.

It is anticipated that this technique will also be applicable to more mundane ceramic situations.

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THE FORMATION OF YBa_2Cu_3Oy THICK FILMS BY PLASMA SPRAYING

Yoshihide Wadayama, Toshimi Matsumoto, Katuzo Aihara, Shinpei Matsuda
Hitachi Research Laboratory, Hitachi Ltd., Hitachi, Japan

The development of improved high Tc superconducting thick films concerns us. Plasma spraying, one of the potential mass production processes, was used to form superconducting thick films of YBa_2Cu_3Oy. Chemical composition, pore volume and superconducting properties of the film was investigated in relation to the plasma spraying conditions such as power supply, gas pressure and YBa_2Cu_3Oy powder size.

The YBa_2Cu_3Oy powder was plasma sprayed onto the substrate at room temperature. The resultant film was predominantly amorphous with a small amount of Y_2O_3 and Y_2BaCuO_5 in the as-deposited condition, depending on the melt quenching conditions. Crystallization of the film took place during post-annealing at 900℃ for 0.5~1h.

The constituent elements, Y,Ba and Cu, were uniformly distributed over the film. The amount of Cu , however, seemed to decrease with excessive melting of the powder, itself related to the powder particle size and power supply. The pore volume could be controlled to less than 5% in area fraction by using fine powder and low gas pressure. The Tc and Jc reached values of 91K and 1120A/cm^2 (at 77K,0T) respectively for some well formed, 100μm thick, YBa_2Cu_3Oy film.

CRYSTAL STRUCTURES OF Tl-(Ba,Sr)-Ca-Cu-O SUPERCONDUCTORS

Atsuko Soeta, Takaaki Suzuki, Tomoichi Kamo,and Shin-Pei Matsuda
Hitachi Research Laboratory of Hitachi Ltd.,Hitachi, Ibaraki 319-12, Japan

We report on the superconductivity and crystal structures in Tl-(Ba,Sr)-Ca-Cu-O (TBSCC) system. In the case of TBSCC system the high Tc phase was easily obtained as a single phase compared with Tl-Sr-Ca-Cu-O and Tl-Ba-Ca-Cu-O systems. As a result we achieved a high superconducting volume fraction, 95% above 100K. Samples of TBSCC were prepared using a conventional powder-mixed method. They were heated at 850~900℃ for 3h in air. The nominal atomic ratio of Tl:(Ba+Sr):Ca:Cu was 2:2:2:3 and 1:2:2:3, where the Ba/Sr ratio was varied at 1/4, 2/3, 1/1, 3/2 and 4/1. The crystallographic transformation was caused by changing the ratio of Ba to Sr in both cases. By the X-ray diffraction and TEM analysis, the crystal structure was determined to be the 2223 structure containing of Tl-O bilayers in the Ba-rich samples, and the 1223 structure containing of Tl-O monolayer in the Sr-rich samples. The ratio of Ba to Sr plays a major role in the determination of crystal structures.

ANISOTROPY OF LATTICE VIBRATION IN ALIGNED $Ba_2EuCu_3O_7$ OBSERVED BY ^{151}Eu MÜSSBAUER SPECTROSCOPY

Tatsuya MURAKI, Masafumi TANIWAKI and Ken-ichi SHIRAMINE
Department of Electronic Engineering, Faculty of Engineering,
Hokkaido University, Sapporo 060, JAPAN

To examine an anisotropy of the lattice vibration in high-Tc superconductor $Ba_2EuCu_3O_7$, we have measured ^{151}Eu Mössbauer spectra of aligned $Ba_2EuCu_3O_7$. In this work we tried to estimate the Debye temperature by measuring the absolute recoilless fraction in aligned samples. Well grinded $Ba_2EuCu_3O_7$ powder was mixed in epoxy and fixed in a magnetic field of 2T to align the c axis. Mössbauer spectra of samples setting the c axis parallel to or perpendicular to the incident gamma ray were taken at room temperature as a function of the Mössbauer nuclei density per unit area. The Debye temperature was obtained from the line broadening with increasing nuclei density and from the dependence of the line area on nuclei density, independently. The Debye temperature in the lattice vibration in the basal plane was higher than that in the lattice vibration parallel to the c axis. The Debye temperature of the non-aligned sample was an intermediate value.

FORMATION OF HIGH-Tc PHASE OF BI-PB-SR-CA-CU-O OXIDE SUPERCONDUCTOR BY MELT PROCESS.

A.Kume[1], K.Tomomatsu[1], H.Fukuda[1], T.Hara[2], H.Ishii[2] and T.Yamamoto[2]

[1]Material Research Laboratory, Fujikura Ltd., Koto-ku, Tokyo 135,Japan
[2]Engineering Research Center, Tokyo Electric Power Company, Chofu-shi, Tokyo 182, Japan.

High Tc phase of Bi-Pb-Sr-Ca-Cu-O, which shows zero resistance at 108 K, has been investigated by Melting process with addition of Pb and later heat treatment. The nominal starting composition was $Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_y$(x=0.25,0.5), the calcined powders in Pt were melted in air at 900-950 °C for 30 min. The solidified products contained the low Tc phase and other non-superconducting phases. And further, the samples were heated at 860-880 °C for more than 100 hours in air, then they became the superconductor with high Tc and low Tc phase, which showed the superconducting transition at 108 K by standard four-probe method. X-ray powder diffraction pattern revealed that they consisted of the high Tc phase of more than 50% at volume ratio. The later heat treatment enhanced formation of high Tc phase by the reaction between the low phase and other phases. Results of the reaction with metal crucible will be also presented.

SUPERCONDUCTING PROPERTIES AND MICROSTRUCTURE OF Ag-SHEATHED $YBa_2Cu_3O_y$ AND SINTERED $YBa_2Cu_3O_y$

Hideo Ishii, Haruhiko Hoshino[+], Tsukushi Hara,
Masaaki Nakamura and Takahiko Yamamoto
Engineering Reseach Center, Tokyo Electric Power Company, Tokyo, Japan
[+]Power and Substation Department, Kandenko, Tokyo, Japan

We have measured some superconducting properties for Ag-sheathed YBCO and only pressed and sintered YBCO and discussed the results in relation to microstructure of these samples observed by SEM. We found for our samples that critical current density of the Ag-sheathed sample is more than five times as large as that of the sintered sample whereas superconducting volume fraction, which is estimated from the magnitude of magnetization considering demagnetizing effect, is larger for the sintered sample. We could not observe significant difference in grain orientation investigated by means of X-ray diffraction. From SEM observation, quite different microstructure could be seen between these two kinds of samples. In the sintered sample, grains contact each other partitioned off by clearly observed grain boundaries which will greatly suppress the magnitude of critical current density. On the other hand, in the case of Ag-sheathed sample, grains seem to be coupling more closely because we could not see clear grain boundaries. This difference is considered to lead to higher critical current density in the Ag-sheathed sample. However, a lot of voids and cracks were observed in the Ag-sheathed sample which are presumably created during sintering process because of different thermal expansion between a Ag sheath and an oxide. Superconducting volume fraction is considered to be smaller for Ag-sheathed sample due to existence of these defects. One can expect still higher critical current density by the reduction of these defects with improved process technique.

PREPARATION OF SUPERCONDUCTING Bi-Sr-Ca-Cu-O RODS BY MELT-QUENCHING AND FLOATING ZONE METHOD

Kazuhiko Sawada, Makoto Hiraoka, Takeshi Shintani,
Takayuki Komatsu*, Kazumasa Matusita*

Central Research Laboratory, Mitsubishi Cable Industries, LTD.,Amagasaki,660 Japan
*Department of Chemistry, Nagaoka University of Technology, Nagaoka,940-21 Japan

Superconducting Bi-Sr-Ca-Cu-O rods were prepared by means of the floating zone method. The influence of starting compositions and growth conditions on superconducting properties and microstructure was investigated.

The feed rods and seeds were prepared by the melt-quenching method. The appropriate amounts of commercial powders of guaranteed reagent Bi_2O_3, Pb_3O_4, $SrCO_3$, $CaCO_3$ and CuO were mixed together and calcined at 800℃ for 12hr in air. The calcined powders were melted in a platinum crucible at 1150 - 1250℃ for 20min in an electric furnace. The melts were pumped up into silica glass tubes with 4.5mm diameter. After the outer glass tubes were removed, the obtained rods were used as the feed rods and seeds. An infrared radiation convergence-type image furnace with two halogen lamps as a radiation source was used for floating zone experiments. The growth rates were 1,2,5 and 10mm/hr.

It was found that the value of T_c increased and the amount of non-superconducting phase decreased with decreasing the growth rate. The 80K phase was dominant and the 110K phase was not detected in as-grown samples. The most highest value of T_c for the as-grown sample was 80K. The microstructure in the sample was composed of large crystals with long pillar shape. These superconducting crystals grew parallel to growth direction. From X-ray diffraction analyses,it was found that the c-axis of the crystals was perpendicular to the growth direction.

PREPARATION OF Ag-SHEATHED Tl-Ca-Ba-Cu-O SUPERCONDUCTING WIRE

H. Takei, Y. Torii, H. Kugai, T. Hikata*, K. Sato*, H. Hitotsuyanagi* and K. Tada
Basic High-Technology Laboratories, * Osaka Research Laboratories,
Sumitomo Electric Industries, LTD.,
1-1-3 Shimaya, Konohana-ku, Osaka, 554 Japan

In the Tl-Ca-Ba-Cu-O system, Tl-O single layered and double layered structures with general formulas $Tl_1Ca_{n-1}Ba_2Cu_nO_{2n+3}$(n=1-6) and $Tl_2Ca_{n-1}Ba_2Cu_nO_{2n+4}$(n=1-4) have been obtained. We fabricated silver sheathed Tl-Ca-Ba-Cu-O superconducting wires using powders of Pb-added $Tl_1Ca_3Ba_2Cu_4O_{11}$ and of $Tl_2Ca_2Ba_2Cu_3O_{10}$ phases whose critical temperatures are the highest among the respective structures. The production process of the wires was cold-working and heat treatment. The transport critical current density J_c at 77K for the wire of $(Tl,Pb)_1Ca_3Ba_2Cu_4O_{11}$ exceeds $10^4 A/cm^2$. There is a tendency for the wire specimens with homogeneous structure of superconducting phases to have high J_c values. The magnetic field dependency of J_c of both wires at 77K shows a two-step decrease in J_c versus B curves. The first and second steps are from zero to 0.1T, and beyond 1T, and the decrease of J_c between 0.1 and 1T is small. The direction of the external magnetic field applied perpendicularly to the transport current against the plane of wire does not influence J_c, because the anisotropic of the wires is small.

Preparation of Superconducting Thick Films of Bi-Pb-Sr-Ca-Cu-O by Gas Deposition of Fine Powder

S.Kashu[1], Y.Matsuzaki[1], M.Kaito[1], M.Toyokawa[2], K.Hatanaka[3], and C.Hayashi[3]

1 Vacuum Metallurgical Co. Ltd., Sambu, Chiba, Japan

2 Tohoku Vacuum Metallurgical Co. Ltd., Hachinohe, Japan

3 ULVAC Japan Ltd., Chigasaki, Japan

Superconducting thick films of Bi-Pb-Sr-Ca-Cu-O material have been successfully made by using of gas deposition with Bi-Pb-Sr-Ca-Cu fine powder of less than 1μm in diameter on MgO substrate.

Shape of deposited fine powder are thin linear films, and thickness of films are 5~200μm.

After heat-annealing of 770℃ for 10hr in air atmosphere, thick films showed Tc(off) of 105K and critical current density of 225A/cm^2 (77K) in zero magnetic field.

Superconductive properties of thick films, such as structure, X-ray diffraction pattern will be reported.

Tape-shaped thick films are deposited on the substrate by using same method.

Width of wide films are 10mm, and this film will be used for superconducting tape materials.

THE CRITICAL CURRENT DENSITY OF Y-RICH Y-Ba-Cu-O SUPERCONDUCTOR BY HALF-MELTED PROCESS

KENJI SHIMOHATA , TOSHIE USHIJIMA , SHOICHI YOKOYAMA , TADATOSHI YAMADA

CENTRAL RESEARCH LABORATORY, MITSUBISHI ELECTRIC CORP., AMAGASAKI, JAPAN 661

It is reported that the melt process improved the critical current density (Jc) of the bulk oxide superconductors. We must form oxide superconductors into optional shape, when we use that for power applications. We applied melt process to the bulk Y-Ba-Cu-O within the range which hold the pressed shape.
The pressed bulk oxide was rapidly heated beyond the melting point and kept a few minutes, typically 1200℃-2mintes, and quenched to room temperature. After this process, that was annealed, typically 900℃-2hours, and slow cooled in oxgen atomosphere. The Jc values of these samples were about 1000A/cm^2(at 0T, 77K). If we anneled longer time, the Jc value dropped for the stoichiometric composition samples, but kept 1000A/cm^2 for the Y-rich one. The growth of the grain of Y-rich compositionsamples differed from the stoichiometric one.

MICROWAVE RESISTANCE OF $YBa_2Cu_3O_y$ CERAMICS CAUSED BY WEAK LINKS

M. Sato, T. Konaka & K. Ishihara
NTT Transmission Systems Laboratories, Tokai, Ibaraki, Japan 319-11

Microwave surface resistance Rs of $YBa_2Cu_3O_y$ ceramics is measured using a TE_{011} resonating cavity of 17GHz in temperature range of 20 K to 300 K. Rs is also measured applying magnetic field (<250 Oe) perpendicularly to the sample surface.

Rs is a sum of Rs_{grain} (Rs of superconducting grains), $Rs_{weak\text{-}link}$ (Rs of weak links between the grains) and Rs_{others} (Rs caused by surface morphology and non-superconducting phases). Temperature dependence of Rs is separated into two temperature regions below Tc. Rs decreases rapidly in narrow region just below Tc. In following lower temperature region, Rs decreases slowly and Rs increase induced by magnetic field is observed.

Rs_{grain} is dominant just below Tc and is thought to be much lower than measured Rs in lower temperature region, where $Rs_{weak\text{-}link}$ is dominant. Using the measured Rs around Tc, the Rs of ideal $YBa_2Cu_3O_y$ ceramics at liq. N_2 temperature is roughly estimated.

PREPARATION OF Bi SYSTEM OXIDE SUPERCONDUCTORS BY MELT GROWTH

K.Hayashi , H.Nonoyama , N.Nagata , H.Hitotsuyanagi

Osaka Research Laboratories , Sumitomo Electric Industries,LTD.
1-1-3 , Shimaya , Konohana-ku , Osaka , 554 Japan

Bi system oxide superconductors were prepared by several method of directional solidification. Crystal structure and superconducting properties (Tc,Jc) were studied as a function of crystal growth and post annealing conditions.

Melt extraction method which is achieved by pulling the BiSrCaCuO melt through the nozzle and solidification at the outlet of the nozzle,was succeeded to obtain 2mm in diameter and 240mm long sample. Crystal structure was well aligned as the growing speed was slower.Tc of 85K and Jc of 173A/cm^2 (77.3K,0T) were obtained.

Horizontal bridgman method from BiSrCaCuO melt was also performed. Crystal alignment was inferior to the other method. So Jc value was very low.

Laser pedestal growth method is the best way in this study to obtain highly aligned structure. Crystal alignment was observed over the growth length. And in the case of Pb addition, we obtained the high Tc phase after annealing.Superconducting properties of Pb added case and Pb not added case were Tc of 87K, Jc of 810A/cm^2(77.3 K,0T)and Tc of 106K and Jc of 1560A/cm^2(77.3K,0T),respectively.

This study was carried out as a part of " R&D program for superconductive generation equipment and materials" under the Moonlight Project of MITI and also being commissioned by NEDO.

PREPARATION OF SUBSTRATES FOR SUPERCONDUCTIVE DEVICES USING Bi-SYSTEM LOW-Tc SINGLE CRYSTALS

K. Takahashi, Y. Nakatani, M. Kamino, T. Yokoo,
Y. Yoshisato and S. Nakano
Functional Materials Research Center, SANYO Electric Co., Ltd.
Hirakata, Osaka, 573 Japan

Single crystals of high-Tc oxide $Bi_2Sr_2CaCu_2O_x$ were successfully grown by a self-flux method in order to realize the possibilities of developing substrates for superconductive devices. Measurement of the electrical resistivity shows that a sharp superconducting transition occurs at 81K with the transition width less than 0.1K. SEM observations indicate that the surfaces of single crystals are very smooth. MgO films were deposited onto the single crystals to fabricate SIS structures by an ion beam sputtering method.

Since the discovery of high-Tc superconducting oxides, there are very few studies on applications of bulk single crystals. However, it can be considered that homogeneity and high density of single crystals are beneficial to the substrates for superconductive devices. Furthermore, superconductivity of substrates themselves can simplify the device structure.

The single crystals were grown from Bi_2O_3, $CaCO_3$, $SrCO_3$. and CuO powders with the cation ratios of 2:1:1:2. Powder X-ray diffraction analysis shows that the crystal is composed of a single $Bi_2Sr_2CaCu_2O_x$ phase. A detailed investigation on the relation between MgO films and substrates such as the interfacial diffusion and the crystallinity of ultra thin films is now being carried out.

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EFFECT OF UNIAXIAL STRESS ONTO THE ELECTROMAGNETIC PROPERTIES OF Bi-Pb-Sr-Ca-Cu-O SUPERCONDUCTORS

Seiji HAYASHI, Kazuyuki SHIBUTANI, Yoshito FUKUMOTO, Rikuo OGAWA and Yoshio KAWATE

Superconducting and Cryogenic Technogy Center, Technology Development Group, Kobe Steel Ltd., 5-5 1-chome, Takatsukadai, Nishi-ku, Kobe 673-02

It is necessary to improve critical current density (Jc) for practical application of high-Tc Bi-Pb-Sr-Ca-Cu-O superconductor. It has been reported that Jc of Ag-seathed Bi-Pb-Sr-Ca-Cu-O superconducting wire could be improved by pressing. We investigate the effect of uniaxial stress onto the Jc, n-value and crosssectional morphology.

The Ag-seathed wires were fabricated by the conventional powders in tube method, formed into wires by swagging, pressing and sintering. Pressing and sintering process was repeated twice, and then Jc was measured by the 4-probe dc method.

Bulk specimens without Ag-seath were fabricated by pelletizing the powders, pressing uniaxially and sintering. Pressing and sintering process was repeated also for these specimens. Then, n-values for these specimens were deduced from the I-V characteristics. Crosssectional morphology were observed by SEM for both types of samples.

It is elucidated that uniaxial stress is effective for the improvement of Jc and n-value. In these good quality specimens, density increase, grain alignment and good contact at the grain boundaries are observed.

RAPID FORMATION OF SUPERCONDUCTING THICK FILM ON Cu-PLATE FROM RAPIDLY QUENCHED Bi-Sr-Ca-M-OXIDE FILM

T.H. Sung, Z. Nakagawa, M. Yoshimoto, H. Koinuma, N. Ishizawa and M. Yoshimura

Research Laboratory of Engineering Materials Tokyo Institute of Technology 4259 Nagatsuta, Midori, Yokohama 227, Japan

High T_c Bi-containing superconductors thick films were rapidly prepared by in situ reaction between the copper oxide and the Bi-Sr-Ca-M-oxide films made by a rapid quenching of their melts. The Bi_2SrCaO_y film with 20 μm thickness was confirmed to be almost in amorphous state. These films were reacted with the copper oxide on the copper substrate at 820-860°C in air. The surface of produced thick film was $Bi_2Sr_2CaCu_2O_x$ superconductor with 00ℓ orientation by heating at 820-850°C for 5 min. Increasing in reaction temperatures or durations results in the formation of excess CuO, and finally in the decomposition of the $Bi_2Sr_2CaCu_2O_x$ phase. The zero resistivity temperature $T_{c(endpoint)}$ exhibited the highest $T_{c(endpoint)}$=76 K for the sample treated at 840°C for 5 min in air. Similar thick superconducting films were prepared by treating even for 1 min, at 840°C.

CONCENTRATION OF CURRENT TO THE SURFACE AND MODIFICATION BY CO_2 LASER FOR OXIDE SUPERCONDUCTOR

H, Nomura*, M. Okutomi*, A.Kitagawa** & T.Onishi*

Electrotechnical Laboratory*
1-1-4 Umezono, Tsukuba, Ibaraki, 305 Japan
Hitachi-Zosen Technical Research Laboratory**
1-3-22 Sakurazima, Konohana, Osaka, 554 Japan

ABSTRACT

There are many issues for oxide superconductors to improve on their properties. Of the issue to solve, both improving their current density and their mechanical strength are important in particular Powder-sintered oxide superconductor have been found difficult to flow superconducting current uniformly to the conductor, but to flow concentrated to the surface of it. Still difficult is a problem that it is poor in mechanical strength. Thus, properties of oxide superconductor are so sensitive to their surface condition that some substantial modifications of the material become very important. Along this line, powder sintered superconductor have been modified by CO_2 laser irradiation. As for the material, $YBa_xSr_{2-x}Cu_3O_y$ was prepared for improving these surface condition, and investigated its superconducting and mechanical properties in according as x value before and after the laser irradiation. Some unique phenomena were found that there was the dependency between current path and the laser irradiated traces. When the current was parallel to the laser traces, superconducting or metallic phases were observed, while it was built up perpendicular to them, superconducting or semiconducting properties were acquired.

THE EFFECT OF PROCESS CONDITIONS IN THE POWDER METHOD ON Jc OF THE Ag-SHEATHED Bi-Pb-Sr-Ca-Cu-O TAPE

Kazutaka Yamamoto, Yutaka Yamada, Satoru Murase, and Yoshimasa Kamisada*

Toshiba R&D Center, 4-1, Ukishima-cho, Kawasaki-ku, Kawasaki, Japan
* Showa Electric Wire & Cable Co.Ltd.,
2-1-1, Odasakae, Kawasaki ku, Kawasaki 210, Japan

Ag-sheathed Bi-Pb-Sr-Ca-Cu-O tapes were fabricated by powder in tube method with pressing. The superconducting properties, especially critical current density (Jc) and flux creep, of the tapes were studied in relation to process conditions.

The calcined powder should be the mixed phase of the low Tc phase (Tc=80K), Ca_2PbO_4 and CuO. Because the high-Tc phase (Tc=110K) was formed through the partial melt reaction of these three phases, which caused large grain growth and thus better connectivity between the grains even after the cold working process such as drawing.

Pressing after heat treatment was further effective to improve the Jc of the tapes. The tape obtained by the process of packing the precursor powder, drawing, rolling, heat treatment, pressing, and final heat treatment, showed higher Jc at 77K of the order of $1000A/cm^2$ than that of the ordinary pelletizing sample of the order of $10A/cm^2$. X-ray diffraction and SEM revealed highly grain-oriented microstructure with the c-plane parallel to the rolling direction. This orientation improved the connectivity and thus the above intergrain critical current. Flux creep behavior for this tape was also improved by this process.

Another promising process for grain-orientation and higher Jc, such as directional heat treatment along the large temperature gradient was also studied.

PYROLYSIS OF ORGANIC PRECURSORS USED TO MAKE SUPERCONDUCTING THIN FILMS

S. Yaegashi, W. C. Moffatt*, H. Murakami, J. Nishino, and Y. Shiohara
Superconductivity Research Laboratory, ISTEC, Tokyo, Japan
*Guest researcher(ETL)

In this study, we have investigated the pyrolysis behavior of metal salts of carboxylic acids of various sorts, including naphthenates, propionates, 2-ethylhexanoates, formates, citrates, acetates, malonates, caprylates,etc.

The carboxylic acid salts of low electronegativity metals generally have higher decomposition temperatures in inert atmospheres than those of high electronegativity metals. There is some tendency for copper salts to decompose over a narrow temperature range, probably because of the ease of reduction of the copper ions: $Cu^{2+} \rightarrow Cu^{1+} \rightarrow Cu^{0}$. Lead and iron 2-ethylhexanoates undergo pronounced two-stage decomposition in inert atmospheres, and bismuth propionate undergoes three-stage decomposition. This is in spite of the absence of a continuous set of valence states for stepwise reduction in the lead and bismuth salts.

The significance of an understanding of precursor pyrolysis and solution characteristics in the production of thin films by spin-coating is described.

PHASE DIAGRAM OF Bi-BASED SUPERCONDUCTORS

T.Noda, T.Izumi, A.Nakamura, and Y.Shiohara
Superconductivity Reseach Laboratory, ISTEC, Tokyo, Japan

It is necessary to understand phase equilibria in the Bi-system to effectively produce superconductors in this system. Experiments were performed using DTA and high temperature microscopy. Equilibrium phases were determined and plotted on a quasi-binary temperature versus composition diagram between the nominal compositions $Bi_2Sr_2Ca_2Cu_3O_y$ (2223, high T_c phase) and $Bi_2Sr_2CaCu_2O_y$ (2212, low T_c phase). We found the liquidus temperature of the compound with 2223 nominal composition to be above 1100°C, and the primary solid phase formed to be Ca-rich. These results contradict those in previously reported phase diagrams, in which the temperature of the liquidus is about 900°C. We also report on the liquidus lines along the composition axis as well as the primary phase corresponding to these lines.

This work has been supported by the R&D Basic Technology for Future Industries through the New Energy and Industrial Technology Development Organization (NEDO).

IMPROVEMENT OF WATER-RESISTIVITY OF HIGH-Tc SUPERCONDUCTIVITY BY Ag2O ADDITION

S. Yoshizawa, Y. Ogawa, K. Yamamoto, Y. Ishikawa, M. Kojima
Central research laboratory, Dowa Mining Co., Ltd.,
Tobuki, Hachioji, Tokyo, 192 Japan

The deterioration of superconductivity in YBCO system occurs rapidly by moisture absorption. The addition of Ag2O into YBCO system improves water-resistivity of superconductivity.

Specimens were prepared by the solid-state reactin method. Appropriate ammounts of Ag2O and calcinated YBCO powder were mixed. The mixture was recalcinated, pulverized, pressed into pellets, and then sintered. Water-resistivity was estimated by measurement of the electrical resistivity of specimens immersed into boiling water.

Immersion of YBCO pellet, which contained no silver, into boiling water for one minute disappeared the superconductivity. By 5wt% and 10wt% addition of Ag2O to specimens retained superconductivity even after the 40 minutes and 1 hour boiling water immersion, respectively.

It was suggested that silver deposited in grain boundary prevents water diffusion into superconducting crystallites.

COMPOSITE SUPERCONDUCTORS FOR UNK MAGNETS

G.K.Zalenskiy, A.P.Golub, A.D.Nikulin, V.Y.Fil'kin, V.P.Kosenko, V.L.Mette, E.V.Nikulenkov, L.V.Potanina, E.I.Plashkin, P.I.Slabodchicov, G.P.Vedernikov, B.V.Yakovlev, N.I.Salunin, I.N.Gubkin, O.F.Shevyakova, Yu.A.Gulyakin, V.A.Vasiliev*, A.V.Zlobin*, K.P.Myznikov*, A.I.Nikulin*.
A.A.Bochvar's All Union Scientific Research Institute for Inorganic Materials, Moscow, USSR
*Institute for High Energy Physics, Serpukhov, USSR

The batches of Ø 0.85 mm wires having 10 mcm and 6.5 mcm in diameter filaments embedded into a copper matrix have been manufactured for UNK superconducting dipoles from alloys HT-50 and HT-55. The optimal modes of thermal - mechanical treatment as well as measures designed to raise the homogeneity of superconducting filaments allowed to obtain the value of the critical current density in wires of up to 3.3×10^5 A/cm^2 for the 5 T field and 4.25 K temperature. The models of superconducting dipoles manufactured from such wires had the bore field induction of at least 5 T without degradation, the tolerable levels of residual fields and ac losses.

PREPARATION OF YTTRIUM BARIUM CUPRATE POWDER BY SOL-GEL METHODS AT LOW TEMPERATURES

H. Murakami, S. Yaegashi, J. Nishino, Y. Shiohara and S. Tanaka
Superconductivity Research Laboratory, ISTEC, Tokyo, Japan

We have succeeded in forming yttrium-barium-cuprate powder using metal alkoxides below 650℃ by sol-gel process which is a technique of preparing pure and homogeneous ceramics at much lower sintering temperature than that in the conventional solid method. No results have reported for a $YBa_2Cu_3O_7$ below 900℃, since $BaCO_3$ is easily formed during pyrolysis of the organic materials.

Generally, in the case of Y, Ba and Cu alkoxides, it is difficult to get homogeneous solutions by the sol-gel method using these alkoxides because of their low solubilities in most organic solvents. In this work, we focussed on the selection of metal alkoxides for starting materials and suitable solvents as well to prepare homogeneous chemical solution. Here we report on the sol-gel synthesis and the formation of superconducting $YBa_2Cu_3O_7$ powder fired only at temperatures below 650℃. This result suggests the sol-gel process is promising for widespread application in the fabrication of films and fibers.

Work supported by R&D of Basic Technology for Future Industries through the New Energy and Technology Development Organization(NEDO).

PREPARATION OF THIN-FILM OXIDE SUPERCONDUCTOR, $Y_1Ba_2Cu_3O_{7-\delta}$ BY FACING TARGET SPUTTERING DEPOSITION TECHNIQUE

Yasuo Takagi, Hideo Yamada, and Noboru Koyama
R & D Labs.-I, Nippon Steel Corp., Kawasaki, Japan

Thin film oxide superconductors, $Y_1Ba_2Cu_3O_{7-\delta}$ were prepared by facing target sputtering(FTS) deposition technique. The FTS* technique is known as one of the most noble sputtering deposition methods in which sputtering plasma can be confined between the sputtering targets, and little damage is introduced into the depositing films by the plasma components like electrons and negative ions.

The films were prepared over a wide range of preparation conditions. Little shifts of the compositions in the prepared films from the target composition were observed throughout the preparation conditions. Among the various conditions the O_2 partial pressure(P_{O_2}) and the substrate temperature(T_s) are important to obtain high quality films. For example, the film deposited at P_{O_2}= 2~4x10^{-2} torr and T_s = 700 °C has T_{c0}=65 K, and complete c-axis orientation perpendicular to MgO (100) substrate.

*Y.Hoshi, M.Naoe and S.Yamanaka:Jpn. J. Appl. Phys., **16**(1977)1715.

POLARIZED PLASMA ANNEALING OF Y-Ba-Cu-O THIN FILMS

H.Shimada, W.Ito, M.Imafuku, S.Ito and S.Matsuda

R&D Laboratories-I, Nippon Steel Corporation,
1618 Ida, Nakaharaku, Kawasaki 211, JAPAN

Superconducting Y-Ba-Cu-O films were prepared by a new annealing method, the *polarized plasma annealing*, of Ba/Y_2O_3/Cu multilayered films formed by sequential electron beam evaporation or amorphous Y-Ba-Cu-O films formed by rf sputtering on MgO(100) substrates.

The essential point of this method is as follows. The film was set in the positive column of the O_2 plasma(frequency:50 Hz) during the annealing. The electric potential of the film was controlled independently of the plasma by using the counter electrode.

The effect of electric potential for the oxidation and phase formation of these films during the annealing was studied. It was found that the plus potential is effective for the oxidization and the minus one promotes the c-axis orientation perpendicular to the plane of the film. The combination of minus and plus potentials can successfully form the superconducting phase having Tc(zero) above 77K.

EFFECT OF COMPOSITION AND DEPOSITION TEMPERATURE DEPENDENCES ON Tc FOR THE RF SPUTTERED Y-Ba-Cu-O FILMS.

N.Akutsu,M.Fukutomi*,H.Takahara,Y.Tanaka*,T.Asano* and H.Maeda*
Corporate R&D Center, Mitsui Mining & Smelting Co.,Ltd.,
Ageo,Saitama,362,Japan
*National Research Institute for Metals,
1-2-1,Sengen,Tsukuba,Ibaraki,305,Japan

We prepared Y-Ba-Cu-O films on heated MgO (100) substrate by rf magnetron sputtering system with three targets, Y_2O_3, $BaCuO_2$ and CuO. The three targets were placed on a circle with equal interval and the substrate was positioned above the center of the circle. In this geometry, the high energied negative ions from the targets did not give harmful effect on the films. The sputtering gas was an argon and oxygen mixture ($Ar:O_2$). The gas pressure was 0.28Pa. The films were in situ post annealed in oxygen atomosphere at the deposition temperature for a few hours. We studied the effect of deposition temperature and composition (target power) on Tc. The Tc was very sensitive to the power of CuO target, not to the power of Y_2O_3 target. The Tc of the nearly stoichiometric films, which were prepared at a wide temperature range (630-700^{o}C), was higher than 80K. We also observed the half value width (w) and position of $Y_1Ba_2Cu_3O_{7-\delta}$ (007) peak from X-ray diffraction. The half value width and peak position of the c-axis oriented films depend on composition and/or deposition temperature, and have a good correlation with Tc. The relation between the half value width and Tc is Tc=89.7±1.0-(23.2±2.0)XW.

IN-SITU PREPARATION OF YBCO THIN FILMS ON SINGLE CRYSTAL LaAlO

Y.HANG;D.P.FAN,S.U.ZHANG AND H.C.ZHANG*;P.H.WU,M.QIAN,B.X.JIANG,Z.J.SUN,S.Z.YANG AND Z.M.JI**
Anhui Institute of Optics and Fine Mechanics,Academia Sinica,
P.O.Box 25,Hefei,Anhui,P.R.China
Department of Physics,Nanjing University,P.R.China*
Department of Information Physics,Nanjing University,P.R.China**

Superconducting YBCO films are successfully prepared by rf magnetron sputtering on single crystal $LaAlO_3$ substrates.The substrate temperature is kept at 650 C during deposition and a subsequent in-situ plasma oxidation treatment is performed at 500 C.The film on $LaAlO_3$ exhibits zero resistance at 90K and critical current density of $1.6X10^4$ A/cm^2 at 77K.

The $LaAlO_3$ substrates are single cryatal wafers cut from the single crystal rod, which is prepared using Czochralski growing process by Anhui Institute of Optics and Fine Mechanics, with diameter 20mm.

In order to evaluate the suitability of $LaAlO_3$ as a substrate for mm wave applications,we measured both the dielectric constant and loss tangent of these substrates at 36 GHz. The results show that the $LaAlO_3$ substrate is clearly favored.

IN-SITU PREPARATION OF SUPERCONDUCTING Y-Ba-Cu-O FILMS BY SEQUENTIAL DEPOSITION USING 40MHz MAGNETRON SPUTTERING

H.Takahashi, N.Homma, S.Kawamoto, H.Kondo, K.Suzuki, and T.Morishita
Superconductivity Research Laboratory, ISTEC, Tokyo, Japan

Superconducting Y-Ba-Cu-O thin films were prepared by sequential deposition using three targets 40MHz magnetron sputtering. This sequential deposition is a very suitable method to control the composition of Y-Ba-Cu-O films, because the deposition time on each target can be precisely changed. These films were prepared on (100) MgO by sputtering $YBa_2Cu_3O_x$, $BaCuO_x$ and Cu targets in this order in a total pressure of 6.5mTorr (Ar+20%O_2).

We present effects of the substrate temperature and deposition time for each target on the crystal structure and electric properties of $YBa_2Cu_3O_{7-x}$. The films prepared at a substrate temperature of 750°C show (00ℓ) reflections and those at 700°C show (110) and (220) reflections in X-ray diffraction.

This work was performed under the management of the R&D of Basic Technology for Future Industries supported by New Energy and Industrial Technology Development Organization.

EPITAXIALLY GROWN SUPERCONDUCTING Y-Ba Cu O FILMS BY MULTI TARGET MAGNETRON SPUTTERING

Masayuki Sagoi, Yoshiaki Terashima, and Tadao Miura

Advanced Research Laboratory, Research and Developement Center, TOSHIBA CORPORATION, 1, Komukai Toshiba-cho, Saiwai-ku, Kawasaki, 210 Japan

Y-Ba-Cu-O films were prepared using a reactive magnetron sputtering method with three targets. The superconducting properties and the structural features of as grown Y-Ba-Cu-O films were evaluated in relation to several deposition conditions. The critical temperature, Tc, was significantly dependent on the distance between the targets and the substrate. Tc's of the film on $SrTiO_3$ (110) substrates increased to more than 80K by optimizing the distance, in spite of very low oxygen partial pressure of 0.3 Pa. Concerning the film on $SrTiO_3$ (100) substrates, the crystalline structure of the film changed from an a-axis orientation to a c-axis one with decreasing the substrate-target distance. The a-axis oriented films were polycrystalline, and their surface layers were composed of small grains. The c-axis oriented films showed an extremely smooth surface, and were found to be single-crystalline from the RHEED observation. The effect of a low-temperature annealing on Tc was also examined. A 550 °C-annealing in an oxygen flow was effective only for the film with the c-axis orientation. In conclusion, the influence of plasma existing above the targets is essential in order to obtain high-quality films.

PREPARATION AND SUPERCONDUCTIVE PROPERTIES OF $YBa_2Cu_3O_y$ THIN FILMS BY COEVAPORATION WITH ECR ION SOURCE

H. OBARA, S. KOSAKA, M. UMEDA and Y. KIMURA, Electrotechnical Laboratory, Umezono 1-1-4, Tsukuba-shi, Ibaraki 305, JAPAN

PREPARATION AND SUPERCONDUCTIVE PROPERTIES OF $YBa_2Cu_3O_y$ THIN FILMS BY COEVAPORATION WITH ECR ION SOURCE
H. OBARA, S. KOSAKA, M. UMEDA and Y. KIMURA, Electrotechnical Laboratory, Umezono 1-1-4, Tsukuba-shi, Ibaraki 305, JAPAN

Superconducting $YBa_2Cu_3O_y$ films have been prepared by coevaporation with ECR ion source in relatively low pressure ($< 5 \times 10^{-5}$ Torr). In the present work, Y, Ba and Cu metal elements were individually evaporated from three effusion cells on MgO substrates with (100) plane, and N_2O gas was introduced to ECR plasma near the substrate. As-deposit films had a orientation with the c axis perpendicular to the substrates, and showed T_c as high as approximately 50 K. After in-situ annealing at low temperature (500°C), T_c of films increased to 80 K without any changes of crystallinity and morphology. Samples were analyzed by in-situ Auger and XPS spectroscopy in a closed system. From Auger analysis, no N was detected in our samples and XPS analysis indicated that N_2O was more effective for the oxidation of samples than O_2. Further, Superconductive properties of samples were measured by SQUID magnetometer. Finally physical properties of thin films and the effects of ECR plasma will be discussed.

FORMATION OF HIGH-TEMPERATURE SUPERCONDUCTING Y-Ba-Cu-O THIN FILM BY IONIZED CLUSTER BEAM

Y. Kawagoe, K. Yamanishi, M. Tanaka, K. Imada*, and K. Yoshizaki*
Manufacturing Development Laboratory, * Materials & Electronic Devices Laboratory, Mitsubishi Electric Corporation, 1-1, Tsukaguchi-Honmachi 8-chome, Amagasaki, Hyogo 661, Japan

The technology of ionized cluster beam (ICB) apparatus with multiple sources and an ozonizer has been developed to form high-temperature superconducting Y-Ba-Cu-O thin films. The films having high critical temperature and critical current density could be obtained at low substrate temperature by utilizing this apparatus. The composition ratio could be controlled by adjusting the evaporation rate of each source independently. The crystallization and oxidation at low substrate temperature could be achieved by controlling the energies of ionized cluster beams and using ozonized oxygen. The concentration of ozone was 6%, the pressure in the chamber was 4×10^{-4}Torr, the deposition rate was 4nm/min, the film thickness was 0.1μm and the acceleration voltages of ICB sources were as low as 300V.

The experimental results obtained to date are as follows:
1) The as-grown film with the critical temperature of 86K was fabricated at the substrate temperature of 650°C.
2) The critical current density of the film was 1.0×10^{6}A/cm^{2} at 77K.

IN-SITU PREPARATION OF Bi-Sr-Ca-Cu-O FILMS BY COEVAPORATION ASSISTED BY ENERGY CONTROLLED ECR OXYGEN ION BEAM

M. KAMEI, I. YOSHIDA, H. TESHIMA, M. NEMOTO, K. SUZUKI, T. MORISHITA

Superconductivity Research Laboratory , ISTEC, Tokyo, Japan

Both substrate precleaning and in-situ preparation of Bi-Sr-Ca-Cu-O films by coevaporation were performed using an ECR oxygen plasma.

Before deposition the substrates were cleaned by the high energy oxygen ion beam. The kinetic energy of ions was controlled by changing the bias voltage of the drift tube. The sputtering rate of a MgO(100) substrate was typically 1A/sec at a bias voltage of 750V. RHEED patterns from MgO surface became streakier after this treatment.

During coevaporation the bias voltage was kept between 250 and 500V so as not to damage films. Bi_2O_3, Sr, Ca and Cu were coevaporated from four separate sources. The 2212 and 2201 mixed phase oriented the c axis normal to the film was grown in-situ. Oxygen partial pressure was 1×10^{-4} Torr in the growth chamber. The growth rate and total film thickness were typically 0.8A/sec and 2500A, respectively. The substrate temperature was changed between 700 and 800C. The crystal structure of Bi-Sr-Ca-Cu-O films was examined by XRD and RHEED. The chemical composition was monitored in-situ by EIES(Electron Impact Emission Spectroscopy) sensors and confirmed by ICP.

This work was performed under the management of the R&D of basic technology for future industries supported by NEDO.

PREPARATION OF $Y_1Ba_2Cu_3O_{7-\delta}$ THIN FILMS BY MBE USING METAL CHELATES

K.Endo, Y.Ikedo[a], S.Hayashida[b], J.Ishiai[c], K.Nakatsuka[d], S.Misawa, and S.Yoshida
Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305, Japan
a)Showa Electric Wire & Cable Co.,LTD., Kawasaki, Kanagawa 210, b)Nippon Sanso K.K., Kawasaki, Kanagawa 210, c)Dowa Mining Co.,LTD.,Hachioji, Tokyo 192 and d)Iwatani Co.,LTD., Chuo-ku, Osaka 541

Thin films with $Y_1Ba_2Cu_3O_{7-\delta}$ superconducting phase have been fabricated on MgO (100) substrates by MBE using β-diketone metal chelate sources for the first time. The use of metal chelate sources in MBE allows a high oxygen pressure compared with that of metal sources because the source temperatures of metal chelates are much lower than those of metals.

The sources were $Y(PPM)_3$, $Ba(PPM)_2$ (PPM: pentafluoropropanoyl pivaloyl methane) and $Cu(DPM)_2$ (DPM: dipivaloyl methane). Each source was loaded into PBN crucible with a shutter and heated at 120, 160 and 45°C, respectively. Oxygen gas was introduced by a stainless nozzle to increase the local oxygen pressure near the substrates. The flow rate of oxygen gas during deposition was about 5 sccm. The oxygen pressure at the position far from the substrates was 10^{-4} torr. MgO substrates were soldered on a molybdenum block with indium metal. The substrate temperature was 600°C. The growth time was 1 hour. The metal composition ratio of the films was determined by inductively coupled plasma spectroscopy (ICP).

As-deposited films were amorphous and insulating. The films were annealed at 900 C for 3 hours and then cooled down to room temperature for 9 hours. The resulting films had $Y_1Ba_2Cu_3O_{7-\delta}$ superconducting phase with the c-axis highly oriented perpendicular to MgO substrates.

In-situ growth of Bi-Sr-Ca-Cu-O Thin Films by Molecular Beam Epitaxy

Yoshimi NAKAYAMA, Ichiro TSUKADA, Atsutaka MAEDA and Kunimitsu UCHINOKURA
Department of Applied Physics, The University of Tokyo, Tokyo, JAPAN

Thin film processes are useful techniques for preparing large single crystals and are of great advantage to preparing the materials with layered structure. To artificially control the structure of oxide superconductor containing Bi, molecular beam epitaxy(MBE) technique with shutter control was developed. The molecular beams were kinetically controlled on the scale of atomic layer and films were deposited layer by layer. A pure ozone gas was used as an oxygen source. As the ozone oxidize metals to their final oxidative state efficiently, a sticking coefficient of Bi metal does not change so much even at high substrate temperature and the back pressure can be maintained as low as 4 10^{-4} Pa during deposition. This low pressure enables us to use in-situ reflection high energy electron diffraction(RHEED) without differential pumping of electron gun. Thin films of $Bi_2(Sr,Ca)_3Cu_2O_y$ have been prepared on MgO(001) and $SrTiO_3$(001). The temperature of substrates was 800°C. Typical superconducting properties for the 80 nm as-deposited films are ρ(300K)=850 $\mu\Omega$ cm, ρ(300K)/ρ(80K)=2.0, Tc(onset)=50 K, Tc(R=0)=30 K and Tc(ρ=0)=30 K. In-situ RHEED observation showed the formation of the perovskite-related structure even at the initial deposition(one unit cell), which suggests that the present method is effective in the growth of oxide containing Bi. Not only the effectiveness but also the hazardousness of the present pure ozone process will be discussed.

PREPARATION AND PROPERTIES OF Y-Ba-Cu-O THIN FILMS ON FLEXIBLE YSZ SUBSTRATES

Shigeru OKUDA, Noriki HAYASHI, Satoshi TAKANO, Hajime HITOTSUYANAGI
Osaka Research Laboratories,Sumitomo Electric Industries, Osaka, Japan
Kiyoshi HASEGAWA, Seiichiro TERAI
Research and Development Group, The Kansai Electric Power Co., Osaka, Japan

Y-Ba-Cu-O thin films were prepared on flexible polycrystalline YSZ (Yittria stabilized zirconia) by RF magnetron sputtering. Sputtering was carried out in an Ar+10%O_2 atmosphere with pressure of $3\times10^{-2} \sim 8\times10^{-2}$ Torr, and the substrates were heated to 700℃. Both as-grown films and post-annealed films had c-axis orientation, and Tc(R=0) of 90.3K was obtained after annealing at 950℃. The films were composed of island-like grains which were partially united with each other. The degree of the union of grains increased as the annealing temperature increased from 850℃ to 950℃. Jc was improved by this union and the highest Jc was $1.2\times10^{4}A/cm^{2}$.

The effect of applied strain on superconducting properties was investigated by bending films. Tc(R=0) increased as the compressive strain increased. On the other hand, Tc(R=0) decreased as the tensile strain increased. Though Jc decreased to 33% of the initial value under a tensile strain of 0.3%, Jc did not decrease under the compressive strain of up to 0.3%. It seems that these results are due to the difference of the thermal expansion coefficients between Y-Ba-Cu-O and YSZ.

CHARACTERISTICS OF SUPERCONDUCTING $YBa_2Cu_3O_{7-x}$ TAPES PREPARED BY CHEMICAL VAPOR DEPOSITION

S. Aoki, T. Yamaguchi, N. Sadakata and O. Kohno,
Material research Laboratory, Fujikura Ltd., 1-5-1, Kiba, Koto-ku,
Tokyo 135, Japan

Application of the high-T_c superconducting materials for conductor has been eagerly expected though the materials has some intrinsic properties like anisotropic current flow and weak links at grain boundaries which may greatly reduce J_c. Thin film fabricating methods are attractive because highly oriented or even single-crystalline films could be obtained. In particular, chemical vapor deposition process is promising because its deposition rate is superior to the other thin film processes. Superconducting $YBa_2Cu_3O_{7-y}$ thin films have been prepared by chemical vapor deposition using beta-diketonate chelates of Y, Ba and Cu on single-crystalline $SrTiO_3$ substrates and metal substrates. Superconducting films were obtained on single crystalline $SrTiO_3$ at tempertures above 750°C. The best films had the zero-resistivity T_c to 89K and J_c of $2.17 \times 10^4 A/cm^2$. According to an X-ray diffraction patterns, the orthorhombic crystal structure oriented c-axis has been confirmed. The films on metal substrates with $SrTiO_3$ buffer layer had Tc at 85K.

PREPARATION OF AS-DEPOSITED SUPERCONDUCTING YBaCuO THIN FILMS ON METALLIC SUBSTRATE BY MAGNETRON SPUTTERING

M.Fukutomi,Y.Tanaka,T.Asano,H.Maeda,National Research Institute for Metals, Tukuba Laboratories,Tsukuba-shi,Ibaraki,Japan and N.Akutsu,K.Hoshino,H.Takahara, Central Research Laboratory,Mitsui Mining & Smelting Co.,Ltd.,Ageo,Saitama, Japan

Superconducting YBaCuO thin films were prepared on metallic substrates in an attempt to fabricate a superconducting tape. Deposition was made by co-sputtering from three oxide targets, CuO,Y_2O_3,and $BaCuO_2$ in an Ar and O_2 mixture atmosphere. The deposition temperature ranged from 600 to 700 C. Most films deposited directly onto the metal substrate exhibited either poor superconducting properties or no superconductivity. We examined, therefore, various buffer layers and found that MgO and BaF_2 buffer layers were a favorable choice to prevent the adverse reaction between the superconducting film and the underlying substrate. Particular attention was given to the preferential resputtering effect due to the bombardment of negative ions during sputtering. The substrate-cathode configuration had a marked effect on the achievement of stoichiometric film composition. All films with good superconducting properties were prepared outside the region of head-on negative ion flux from each target. Most films obtained in the present study were between 0.7 and 1.5 μm in thickness and oriented polycrystalline materials. The highest zero resistance temperature obtained so far of the YBaCuO thin films on a metallic tape was 84.0 K in its as grown state, and a critical current density was $2x10^3$ A/cm^2 at zero field and 77.4 K, which will be raised by optimizing the deposition conditions.

FORMATION METHOD OF YBCO THIN FILMS WITH LARGE CRITICAL CURRENT Ic

Hiroshi Kajikawa, Yoshito Fukumoto, Seiji Hayashi, Rikuo Ogawa, Yoshio Kawate
Superconducting & Cryogenic Technology Center, KOBE STEEL, LTD.,
1-5-5, Takatsuka-dai, Nishi-ku, Kobe, 673-02, Japan

The effect of the metallic composition and the heat-treatment temperature on the superconducting properties of YBCO thin films was systematically investigated. The films were deposited by the RF diode sputtering method on $SrTiO_3$(100), MgO(100) and $LaAlO_3$(100) substrates in an amorphous state and crystallized into the orthorhombic 123 phase using a two-step heat-treatment in an oxygen atmosphere (the first step: 850-920°C for 25 minutes; the second phase: 550°C for 120 minutes).

Good superconducting properties of Tc ~ 90 K and Ic>2 A were repeatedly obtained in the films with the Cu-poor compositions of $Y_1Ba_{2-2.3}Cu_{2.3-2.7}Ox$, deposited on $SrTiO_3$(100) substrates at a temperature <350°C and at a RF power~300 W, and then heat-treated at 880 °C in the first step.

In these films, it was observed from the x-ray diffraction pattern and the scanning electron micrograph that the insulating second phase $BaCuO_2$ was reduced and the mixture of a-axis and c-axis oriented grains were closely arranged. It was also found that the Ic became abruptly large as the temperature was decreased slightly below the Tc. These results might suggest that the high-Ic films were comprised of the strongly coupled crystal grains that formed the macroscopic current path.

PREPERATION OF SUPERCONDUCTING Ti DOPED Y-Ba-Cu-O FILMS ON METAL SUBSTRATES WITH A THIN BUFFER LAYER

J. SHINOHARA, K. INOUE*, M. NOZAWA*, S. IDO*

Research Institute, Ishikawajima-Harima Heavy Industries Co.,Ltd.
3-1-15, Toyosu, Koto-ku, Tokyo, 135 JAPAN

*Department of Electrical Engineering, Faculty of Engineering,
Saitama University, Shimo-Ookubo 225, Urawa, 338 JAPAN

Ti-doped Y-Ba-Cu-O superconducting films were prepared on single crystals and metal substrates by RF magnetron sputtering method. Post-growth annealing was carried out in an oxygen atomosphere. Ni base superalloy Inco-718 was used successfully as the substrate for high-Tc superconducting thin films with a thin buffer layer of MgO. The films exhibit sharp transition profile of the resistivity. The high-Tc superconducting phase of the film are higher stable than Ti-free sample. A superconducting transition was obtained Tc(onset)=83K. The film composition was estimated by inductively coupled plasma-emission spectrometry (ICP), and it was found that the Ti-Y-Ba-Cu ratio was 0.02-0.13 :1:2:3. The crystalline structure of the film and the characteristics of buff erlayer will be disscussed.

ORIENTED $YBa_2Cu_3O_{7-x}$ SUPERCONDUCTIVE THIN FILM GROWTH ON METALLIC SUBSTRATE BY ICB DEPOSITION METHOD

H.Yoshino, M.Yamazaki, T.D.Thanh, T.Yamashita and K.Ando

Advanced Research Laboratory,Research and Development Center,TOSHIBA CORPORATION
1,Komukai,Toshiba-cho,Saiwai-ku,Kawasaki,210, JAPAN

Oriented $YBa_2Cu_3O_{7-x}$ superconductive thin film on silver substrate was prepared by oxygen plasma-assisted ICB(Ionized Cluster Beam) deposition method.

Silver,nickel,nichrome and Inconel alloys were investigated as candidate substrate without any buffer layer. The deposition was done in radio frequency excited oxygen plasma at a substrate temperature of about 650C and the films were cooled slowly in oxygen plasma. Only the film on silver substrate showed high orientation of (001) plane of $YBa_2Cu_3O_{7-x}$. The acceleration for the cluster is very effective for the improvement of its orientation and crystalization.

This work was performed as a part of R&D on Superconducting Technology for Electric Power Apparatus" under the Moonlight Project of Agency of Industrial Science and Technology,MITI,being consigned by New Energy and Industrial Technology Development Organization(NEDO).

OXIDE SUPERCONDUCTOR BSCCO FILMS PREPARED BY THE RAPID MELTING AND RESOLIDIFICATION OF CERAMIC POWDER PROCESS USING CO2 LASER BEAM.

K. Agatsuma, F. Uchiyama, K. Tsukamoto,
T. Ohara and T. Yanagisawa

Electrotechnical Laboratory,Tsukuba,Ibaraki,Japan

The thin film growth techniques of new high Tc oxide superconductors are really important especially for the electronic device applications. Also the production techniques of new high Tc superconducting wires or tapes are intensely desired to be developed for energy applications. We have been developing The Rapid Melting and Resolidification of Ceramic Powder Using Laser Beam Process. A high power CO2 laser beam is applied to an extremely small quantity of BSCCO fine powder which is dropped from a micro feeder system and deposited onto a substrate. This process has a remarkable advantage of rapid growth of the thickness of these ceramic superconductors to make a superconducting tape rather than other techniques, for example, sputtering or chemical vapor deposit process. We have successfully made BSCCO films on Y 8% stabilized ZrO2 (YSZ) and SrTiO3 substrate by this Rapid Melting and Resolidification of Ceramic Powder using Laser Beam process. This film has about 85 K superconducting onset temperature. The results of investigations of these films by using energy dispersive X-ray analysis (EDX), wave length dispersive X-ray analysis (WLDX) and scanning electron microscopy (SEM) examinations are presented in this paper.

SUPERCONDUCTING PROPERTIES OF ARTIFICIALLY SUPERSTRUCTURED FILMS COMPOSED OF NITRIDE MATERIALS

Mitsugu Sohma, Kenji Kawaguchi, and Shigemitsu Shin
National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305, Japan

We are interested in artificially superstructured films (ASF's) composed of both superconducting and magnetic materials. Because it is a attractive study in the field of superconductivity whether ferromagnetism and superconductivity can coexist or not. The ASF is a good model sample for this purpose. Since nitride ASF's have high corrosion resistance and good thermal stability in general, it is easy to handle. The combination of niobium nitride (NbN) and iron nitride (FeN) was chosen in this work. In transition metal nitrides, NbN has been reported to have fairly high Tc(17.3K) and FeN is a well known ferromagnetic material. We prepared NbN/FeN ASF's on MgO<100> substrates by an alternate reactive deposition method. From X-ray diffraction patterns, it was appeared that B1 type NbN was crystallized only when the samples were prepared in nitrogen atmosphere activated by r.f. plasma. The NbN layers had <100> preferred orientation normal to the substrates. The artificial superstructure was confirmed when the substrate temperature was below 300°C.

The investigation of detailed structural properties and their physical properties under the various deposition conditions has been in progress.

COMPLEX SUSCEPTIBILITY IN SINGLE-CRYSTAL $YBa_2Cu_3O_{7-X}$ THIN FILMS

Hiroshi Yasuoka, Hiromasa Mazaki, Kazunuki Yamamoto,[*] Kazuto Hirata,[*] Takahito Terashima,[**] Kenji Iijima,[*] Katsuhiko Hayashi,[*] and Yoshichika Bando[**]

Department of Mathematics and Physics, The National Defense Academy, Yokosuka Japan

[*]Research Institute for Production Development, Kyoto Japan

[**]Institute for Chemical Research, Kyoto University, Uji Japan

Higher-harmonic susceptibility was measured for single-crystal $YBa_2Cu_3O_{7-X}$ thin films located in ac magnetic field perpendicular to the film plane. We found that the complex higher-harmonic susceptibility has nonzero values in the region of superconducting transition in terms of fundamental susceptibility. The nonzero higher harmonic susceptibility indicates that the magnetization responses nonlinearly. This nonlinear response and the nonzero imaginary part of the fundamental susceptibility suggest that the magnetization curve traces hysteresis loop. These must be caused by the appearance of the obstruction of vortex motion.

UV LIGHT IRRADIATION EFFECTS ON $Bi_2Sr_2Ca_1Cu_2O_x$ SUPERCONDUCTING THIN FILMS

A. ENOKIHARA, S. KOHIKI*, K. SETSUNE, and K. WASA
Central Research Laboratories, Matsushita Electric Industrial Co. Ltd., Moriguchi, Osaka, 570 JAPAN.
*Matsushita Technoresearch Inc., Moriguchi, Osaka, 570 JAPAN.

UV light irradiation effects on $Bi_2Sr_2Ca_1Cu_2O_x$ superconducting thin films were investigated. The films 110 nm thick were prepared on MgO single-crystal substrates at 580 °C by means of rf magnetron sputtering. UV light emitted from a low pressure mercury lamp of 180 W was irradiated onto the film sample. The sample was set in helium gas of about 0.5 Torr to eliminate interaction with ozone. After the irradiation of 50 min, zero-resistance temperature and critical current density at 4.2 K of the film were decreased from 56 K to 26 K and from 2.2×10^5 A/cm^2 to 1.0×10^4 A/cm^2, respectively. And the resistivity at room temperature was increased twice. These properties were improved with oxygen annealing at 700 °C. However, no remarkable change in crystal structure was observed from the X-ray diffraction analysis. Optical absorption spectra of the film had a peak at around 250 nm wavelength, which corresponds to the excitation energy of electrons in the Cu d-O p bonding orbital.

From these results, we speculate as follows. The UV light excited electrons in the Cu-O bonding orbital to induce vacancies in the oxygen site of the Cu-O plane so that the superconducting properties were degraded. These vacancies were filled by the annealing in oxygen.

FABRICATION OF BiSrCaCuO/FERROMAGNET LAYERED THIN FILMS

T. MATSUSHIMA*, Y. ICHIKAWA, H. ADACHI, S. HATTA, K. SETSUNE and K. WASA
Central Research Laboratories, Matsushita Electric Industrial Co. Ltd., Yagumo-nakamachi 3-15, Moriguchi, Osaka 570, Japan
*Semiconductor Research laboratory, Matsushita Electric Works, Ltd. 1048, Kadoma, Osaka 571, Japan

The study of the interaction between superconductivity and magnetism has attracted much attention. In previous reports of superconductor/ferromagnet superlattices such as V/Ni, V/Fe and Al/EuO, various attractive phenomena of superconductivity have been observed. These phenomena are probably caused by the proximity effect.

In this study, we report preliminary results of structure and superconducting properties of $Bi_2Sr_2CaCu_2O_y/NiFe_2O_4$ layered thin films. The $NiFe_2O_4$ compound is a ferromagnetic insulator with Curie temperature of 858 K and with spinel structure. The layered thin films were deposited by rf magnetron sputtering. At the first step, $NiFe_2O_4$ films(1000Å) were deposited on (100) MgO at the substrate temperature of 700°C. X-ray diffraction pattern of $NiFe_2O_4$ films showed a very high degree of orientation with the a-axis normal to the film plane. The magnetization measurement on films showed that a easy axis of the magnetization was normal to the film plane and a value of saturation magnetization at room temperature was about 320 emu/cc. This value corresponds to that of bulk material. Subsequently $Bi_2Sr_2CaCu_2O_y$ films(2000Å) were deposited on $NiFe_2O_4$ films at the substrate temperature about 600°C in order to prevent interdiffusion of atoms between $Bi_2Sr_2CaCu_2O_y$ and $NiFe_2O_4$ films. X-ray diffraction pattern of the $Bi_2Sr_2CaCu_2O_y$ films deposited on $NiFe_2O_4$ films showed a high degree of orientation with the c-axis normal to the film plane and showed that a onset superconducting temperature was about 80K.

Bi BASED OXIDE SUPERCONDUCTING THIN FILM PREPARED BY CVD METHOD.

Kenichi Saikusa, Tadashi Sugihara, Takuo Takeshita.
Central Research Lab. Mitsubishi Metal Corporation.
330 Kitabukuro 1-297, Omiya, Saitama, Japan.

BiSrCaCuO system oxide superconducting thin films were prepared on MgO single crystal by CVD method using organo metallic complexes as starting gas sources.

A thin film was deposited at substrate temperature of 800°C and under total pressure of 15 torr, and it is the 2212 phase and has a C-axis oriented mosaic microstructure. It's critical temperature is 70K.

Deposition conditions such as substrate temperature, oxygen partial pressure and cooling rate are discussed with regard to preparation of pure 2212 phase.

LOW TEMPERATURE GROWTH OF $YBa_2Cu_3O_x$ THIN FILMS BY METALORGANIC CHEMICAL VAPOR DEPOSITION

Keiichi Kanehori, Nobuyuki Sugii, Kazushige Imagawa and Katsuki Miyauchi

Central Research Laboratory, Hitachi, Ltd., Kokubunji, Tokyo 185, Japan

Metalorganic chemical vapor deposition (MOCVD) is considered one of the most desirable method to grow superconducting $YBa_2Cu_3O_x$ thin films. However, the typical deposition temperature is such a high temperature as interdiffusion or reaction between film and substrate proceeds. Therfore, concerted efforts are required to lower deposition temperature to apply MOCVD in electronics field. This paper reports effects of deposition condition on crystallographic and electrical properties of Y-Ba-Cu-O thin films.

Thin films were grown by a low pressure MOCVD apparatus, using tetramethyl -heptanedione complexes of Y, Ba and Cu as source materials. The grown films were cooled in an O_2 atmosphere at a pressure of 760mmHg.

X-ray diffraction analysis of the grown films showed that thin films grown in the temperature range from 600℃ to 800℃ had the orthorhombic $YBa_2Cu_3O_x$ structure. The lattice constants of the films were defined as a=3.82Å, b=3.90Å, c=11.7Å. Crystallinity of the films, especially ordering along the c-axis, deteriorated with decreasing deposition temperature. However, crystallinity can be improved by decreasing deposition rate. Thin films grown at a deposition rate less than 0.5 μm/h showed distinct (00ℓ) peaks, even though deposition temperature was 700℃. Thin films, with good ordering along the c-axis, indicated good electrical properties. A superconducting $YBa_2Cu_3O_x$ thin film with a Tc(onset) of 86K and a Tc(R=0) of 83K was grown at 700℃.

A 110-K Phase BiSrCaCuO Thin Film Grown by Halide CVD

M. Ihara, H. Yamawaki, T. Kimura and H. Nakao

Fujitsu Laboratories Ltd., Atsugi

As deposited superconducting BiSrCaCuO thin films with 110-K phase and good morphology were grown on MgO substrates by chemical vapor deposition (CVD) using metal-halide sources and oxygen gas. The X-ray diffraction pattern for 0.1 to 0.3 μm thick as-grown superconducting layers indicated a peak of 110-K phase BiSrCaCuO crystal. The lattice constant for the C-axis plane was estimated to be 3.6 nm. Resistivity at 300-K and critical temperature were ρ=1 to 3 mΩ-cm and Tc=89-K to 97-K for these layers. Critical current was Jc=2 x $10^5/cm^2$ at 10-K for 10 to 50 μm wide BiSrCaCuO layer. The layer composition was $Bi_2Sr_{1.5\text{-}3}Ca_{1\text{-}1.5}Cu_{3\text{-}4.5}O_x$ by X-ray fluorescence analysis (XFA).

BiSrCaCuO superconducting layers were grown on MgO (100) substrates using $BiCl_3$-SrI_2-CaI_2-CuI-O_2 in an open-tube CVD system. The MgO (100) substrate was 30 mm x 30 mm. Before growth, substrates were etched, for example with HCl (90) + H_2O_2 (10). Halide source temperatures were $BiCl_3$=150-170°C, CuI=450-480°C, SrI_2=800-850°C, CaI_2=800-850°C. MgO substrate temperatures were T=750-800°C. The growth rate of BiSrCaCuO layers was 0.5-1.0 nm/min. This paper discusses CVD technique and characteristics of the as-grown BiSrCaCuO layers.

PREPARATION OF $YBa_2Cu_3O_{7-y}$ SUPERCONDUCTING FILMS BY THE ORGANIC TRANSPORT-CHEMICAL VAPOR DEPOSITION

S. Matsuno, F. Uchikawa and K. Yoshizaki
Materials & Electronic Devices Laboratory, Mitsubishi Electric Corporation,
1-1-57 Miyashimo, Sagamihara, Kanagawa 229, Japan

PREPARATION OF $YBa_2Cu_3O_{7-y}$ SUPERCONDUCTING FILMS BY THE ORGANIC TRANSPORT-CHEMICAL VAPOR DEPOSITION
S. Matsuno, F. Uchikawa and K. Yoshizaki
Materials & Electronic Devices Laboratory, Mitsubishi Electric Corporation,
1-1-57 Miyashimo, Sagamihara, Kanagawa 229, Japan

High Tc $YBa_2Cu_3O_{7-y}$ superconducting films were prepared by metalorganic chemical vapor deposition method using a new source transport technique (Organic Transport-Chemical Vapor Deposition : OT-CVD), to increase deposition rates of the films. β-diketonates of Y,Ba and Cu were adopted as source materials. Ar and organic vapor (tetrahydrofuran) were used as carrier gases. Metastable addition products formed between the vapor and source materials were thought to be transported smoothly to the reactor. This method could give a major decrease of the sublimation temperature of Ba source. Deposition rate of the film was achieved over 20μm/hr. The superconducting zero-resistance temperature of the film was 84K. The film was shown to have a smooth surface and a dense body. This work was performed as a part of " R&D on Superconducting technology for Electric Power Apparatuses " under the Moonlight Project of Agency of Industrial Science and Technology, MITI, being consigned by New Energy and Industrial Technology Development Organization (NEDO).

THIN FILM FABRICATION OF BSCCO SUPERCONDUCTORS USING MOCVD

T.SUGIMOTO, S.YUHYA, Y.YAMADA, H.HAYASHI, K.KIKUCHI,
M.YOSHIDA,
K.SUGAWARA, Y.SHIOHARA

Superconductivity Reserch Labolatory, ISTEC, Tokyo, Japan

MOCVD is a promising thin film fabrication process due to its high producibility and precise controllability. However, the stability of metalorganic (MO) source compounds for oxide superconductors is very weak. Precise control of film thickness and composition has not been realized.

We have succeeded in constructing an MOCVD apparatus with high reproducibility of films improving line-heatings for the uniformity of MO transport at relatively low vaporization temperatures for MO sources. Superconducting BSCCO thin films were prepared on (100) single crystal MgO substrates. The films were characterized by X-ray diffraction (XRD), four-probe resistivity mesurement, scanning electron microscope (SEM), and inductively coupled plasma chemical analysis (ICP). The XRD pattern of superconducting BSCCO thin films prepared at 850°C showed only (00l) reflections originating from $Bi_2Sr_2CaCu_2O_x$ (80K phase) and $Bi_2Sr_2Ca_2Cu_3O_x$ (110K phase). The as-grown BSCCO thin films showed an onset temperature of 107K and zero-resistivity temperature of 78K. The relation between the growth temperature and the deposition rate of components of a BSCCO thin film was also investigated.

IN-SITU GROWTH OF Bi-Sr-Ca-Cu-O FILMS WITH HIGH T_c SUPERCONDUCTING PHASE BY MOCVD

K.Endo, S.Hayashida[a], J.Ishiai[b], Y.Ikedo[c], K.Nakatsuka[d], S.Misawa, and S.Yoshida
Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305, Japan
a)Nippon Sanso K.K., Kawasaki, Kanagawa 210, b)Dowa Mining Co.,LTD., Hachioji, Tokyo 192, c)Showa Electric Wire & Cable Co.,LTD., Kawasaki, Kanagawa 210 and d)Iwatani Co.,LTD., Chuo-ku, Osaka 541

As-grown Bi-Sr-Ca-Cu-O films with high T_c superconducting phase were prepared on MgO (100) substrates by MOCVD. In order to increase the amount of the high T_c phase in the films, various growth conditions for MOCVD were examined.

The source materials were triphenyl bismuth $Bi(C_6H_5)_3$, bis(-2,2,6,6-tetramethl-3,5-heptanediono)-strontium $Sr(DPM)_2$, -calcium $Ca(DPM)_2$ and -copper $Cu(DPM)_2$. MgO substrates were put on a graphite susceptor coated with SiC and then heated inductively. The pressure of the reactor was kept at 50 Torr during the growth.

At the substrate temperature of 800°C, the films with T_c(onset)=110 K and T_c(end)=70 K were obtained without postannealing. The X-ray diffraction patterns show that the films were composed of a mixture of the low T_c and high T_c phases with the c-axis oriented perpendicular to the substrate. The SEM studies revealed that the surfaces of the as-grown films are smoother than those of the annealed films.

The films with c=141.8 Å were also obtained without postannealing. This lattice constant just corresponds to $3c_H + c_L$, where c_H and c_L denote the lattice constant of high T_c and low T_c phase, respectively. This implies the possibility of the formation of the superlattice composed of the stack of three layers of the high T_c phase and one layer of the low T_c phase.

SYNTHESIS OF Bi-Pb-Sr-Ca-Cu-O THIN FILMS BY PbO VAPOR ANNEALING

Hirotoshi Nagata, Eungi Min, Shouichi Hashiguchi,
and Kyouichi Shibuya
Sumitomo Cement Co. Ltd., Central Research Laboratory, 585 Toyotomi-cho, Funabashi, Chiba 274, Japan.

Lead ions, in Bi-Sr-Ca-Cu-O systems, acts as feasible dopant to form crystal structures of superconductors such as $Bi_2Sr_2Ca_2Cu_3O_x$ (2223) phase. However, thin film synthesis of these materials with sputtering and post-deposition annealing have difficulties in doping proper amounts of Pb into the film, because Pb and PbO volatilize from the film during the synthesis process. To solve this problem, we doped Pb ions into the unleaded films sputter-formed on MgO or $SrTiO_3$ substrates by means of PbO vapor when its annealing at above 800 °C. Auger and electron probe microanalysis, and X-ray diffractometry showed that Pb ions could penetrate through the film and help (2223) phase dominating in the multipase film. Amounts of doped Pb was measured to be about Pb/(Bi+Pb)=0.1 if Pb ions substitute some of Bi sites. This annealing with PbO vapor was also effective in synthesis of bulk (2223) ceramics, but excess PbO vapor formed Ca_2PbO_4 with decomposing of superconductor phases.

The film 400nm thick on MgO annealed with PbO vapor at 860°C exhibited zero-resistivity at 103K, although the film was consisted of multiphase. The film on $SrTiO_3$, however, did not achieve superconductivity because of Ca loss from the film by formation of calcium titanates.

AS GROWN Y-Ba-Cu-O THIN FILMS WITH FINE GRAINS AND THE FABRICATION OF THE SUPERCONDUCTING LINES

E. Ohno, M. Nagata, H. Shintaku, H. Nojima, and M. Koba

Sharp Corporation, Central Research Laboratories,
2613-1 Ichinomoto-cho, Tenri,
Nara 632
JAPAN

Superconducting thin films of $Y_1Ba_2Cu_3O_{7-x}$ have been prepared by rf magnetron sputtering using the single target with the stoichiometric composition. The films were grown on the substrate(10×20 mm^2) placed outside the upper region of the target. We obtained the films with fine grains 0.2 μm in average size and the smooth surface. The films without post annealing show a zero resistance at around 80 K. The dependence of the crystal structure and the superconducting properties on the position of the substrate was investigated. The c-axis of the specimen was highly oriented normal to MgO(100) plane in the wide area(10×40 mm^2). The length of the c-axis, however, depends on the position of the substrate. The superconducting lines having 2 μm width and 500 μm length were fabricated from the films of 200 nm thickness by chemical etching without serious degradation.

IN SITU FORMATION OF Bi-SYSTEM THIN FILMS BY RF MAGNETRON SPUTTERING FROM Pb-DOPED THREE TARGETS

Ken'ichi Kuroda, Kazuyoshi Kojima, Masami Tanioku, Kazuo Yokoyama[+] and Koichi Hamanaka

Central Research Laboratory, [+]Material and Electronic Device Laboratory, Mitsubishi Electric Corporation, Amagasaki, Japan

Superconducting BiSrCaCuO thin films have been formed on MgO(100) substrate by RF magnetron sputtering from three targets: $Bi_{2.4}Pb_{0.6}Sr_2Ca_2Cu_3O_x$, $Bi_{1.6}Pb_{0.4}Sr_3Ca_3Cu_3O_x$, and $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_{4.5}O_x$. The three targets were simultaneously discharged and the substrate was circulated passing alternately over each target; the substrate temperature was 660°C and the sputtering gas was O_2 at 300 mTorr. The chemical composition of the metal elements was precisely controlled by adjusting the staying time of the substrate over each target. No trace of Pb was detected in the film formed at 660°C by ICP analysis.

The as-grown film with optimum composition had the resistivity drop at 108 K and the zero resistivity at 72 K. On the other hand, the film with the in situ annealing process had the resistivity drop at 115 K and the zero resistivity at 83 K; the annealed film was made under the same sputtering conditions and was kept at the same substrate temperature and at gas pressure for 5 hours after deposition. It is concluded from this experimental result that the in situ annealing process improves the superconducting properties.

PROPERTIES OF SPUTTER-DEPOSITED Y-Ba-Cu-O THIN FILMS

Michihito MUROI , Yuko OKAMURA, Takeshi SUZUKI, Koichi TSUDA, Megumi NAGANO, and Kazuo MUKAE
Fuji Electric Corporate Research and Development Ltd.
2-2-1 Nagasaka, Yokosuka, Kanagawa, Japan 240-01

Thin films of Y-Ba-Cu-O (YBCO) have been prepared on MgO(100) or $SrTiO_3$(100) substrates at 650°C by rf-planar magnetron sputtering using a single oxide target. A metal mask was placed between the target and the substrate to prevent the direct bombardment of the growing film by high-energy particles. Two types of masks, a ring and a disk, were examined. Both masks were designed so that any point on the substrate could not see the erosion area of the target.

The use of a mask allowed the fabrication of YBCO films with c-axis orientation and rather short lattice constant c_0 of about 11.8Å regardless of the sputtering gas pressure, while the deposition with no mask caused the c_0 to enlarge to 12Å at the lower gas pressure. Moreover, the XRD peaks as well as the rocking curves were sharper for the films deposited with the mask than for those deposited without it, showing the former had more excellent crystallinity than the latter. The Tc's of the films were 50-65K after annealed at 500°C in oxygen. However, an apparent resistance drop, which indicated the existence of the high-Tc phase, was observed at about 80K for those on $SrTiO_3$ substrates. The fraction of the high-Tc phase increased by raising the substrate temperature to 700°C.

The manner in which the deposition rates varied with gas pressure and even the film compositions depended on the shape of the mask. These phenomena were well explained by using the idea of the diffusion front which was formed by the thermalized atoms and from which they were transported toward the substrate by thermal diffusion.

AS-DEPOSITED SUPERCONDUCTING Bi-Sr-Ca-Cu-O THIN FILMS PREPARED BY RF MAGNETRON SPUTTERING

Kazushige Ohbayashi*, Shigeru Suzuki, Yoshiaki Takai and Hisao Hayakawa
*NGK Spark Plug Co.,Ltd., Nagoya University

As-deposited superconducting thin films of the Bi-Sr-Ca-Cu-O system were successfully prepared on MgO(100) substrates by a three targets rf magnetron sputtering with a regulated shuttering technique [targets : $Bi_{2.0}Sr_{1.6}Cu_{0.9}O_x$, $Ca_{1.0}Cu_{1.0}O_x$ and Bi_2O_3]. Shuttering was employed in order to control the chemical composition of the films and to help form the desired crystal structure with c-axis in the growth direction.

The films which were prepared without using shuttering, showed semiconductor-like behaviors and no c-axis orientation.

X-ray diffraction patterns from the as-grown films deposited at the substrate temperatures in the range of 580-660^{o}C, showed the low-Tc phase and all the peaks indicated can be indexed as (002n) to a 30A unit cell. The superconducting transition temperature(Tc zero) of the film deposited at 660^{o}C was 70K with a thickness of 300nm. These films had a smooth surface and no segregation of the constituent elements.

FORMATION MECHANISM OF AS-DEPOSITED EPITAXIAL $YBa_2Cu_3O_X$(X=6-7) THIN FILMS IN LASER DEPOSITION

M.Ohkubo, T.Kachi, T.Hioki and J.Kawamoto
Toyota Central Research and Development Labs., Inc.
Nagakute-cho, Aichi, 480-11, Japan

By laser deposition, one can prepare as-deposited $YBa_2Cu_3O_X$ superconducting thin films without post-annealing. However, to achieve high *Tc* and high *Jc*, post-annealing is frequently indispensable. In particular, it has been often observed that a rapid cooling following the deposition results in a formation of non-superconducting or low *Tc* thin films. This is obviously caused by oxygen deficiency with x considerably less than 7. On the other hand, it was reported that a rapidly cooled thin film had a high *Tc* and a high *Jc*. Furthermore, in-situ growth of superconducting thin films with a high oxygen-content was also reported. These results are seemingly contradictory.

In this paper, we study the formation process of the as-deposited epitaxial $YBa_2Cu_3O_x$ thin films by ArF-excimer-laser deposition. After the deposition, the thin films were rapidly cooled in oxygen atmosphere at controlled pressures in a deposition chamber. As the oxygen pressure increases, the oxygen content x increases from 6 to 7. The relation between the x and the oxygen pressure is almost consistent with that for a powder sample which is in a thermal equilibrium. Therefore, we conclude that the thermal-equilibrium oxygen-content regulates the oxygen content in the as-deposited thin films. It is proposed that the $YBa_2Cu_3O_x$ films with x of near 6 may grow during the deposition, and the appropriate amount of oxygens, which depend on the oxygen pressure, diffuse into the films during the subsequent cooling process. The best film after the rapid cooling has a *Tc* with zero resistance of 88 K and a *Jc*(77 K) of 5.5×10^5 A/cm^2.

PREPARATION of Y-Ba-Cu-O SUPERCONDUCTING FILMS by EXCIMER LASER ABLATION

Noriyuki Yoshida , Mari Kubota , Satoshi Takano , Ken-ichi Sato ,
Hajime Hitotsuyanagi , Maumi Kawashima
Osaka Research Laboratories,Sumitomo Electric Industries,Osaka,Japan.
Tsukushi Hara , Hideo Ishii , Takahiko Yamamoto
Enginieering Research Center,Tokyo Electric Power Company,Tokyo,Japan.

Y-Ba-Cu-O films were deposited on MgO and $SrTiO_3$ substrares by KrF excimer laser ablation of a stoichiometric 1-2-3 target. The substrate temperature was kept at 700 ℃～800 ℃ and the oxygen pressure during the deposition was chosen in the range of 0.01～1Torr.The target was irradiated at 45° angle of incidence with the laser ,whose energy density on the target is 1.5～2.5 J/cm^2. The laser was operated at a repetition rate of 1 ～5Hz. The total number of laser shots was approximately 2000. The deposition rate was in the range of 40 ～2200 Å / min..

As-deposited films even at the deposition rate of 2200 Å/min. have been found to have the almost perfect c-axis orientation normal to the substrate surface using X-ray diffraction measurements. Scanning electron microscope observations reveal that as-deposited films have mirror-like surface at relatively low deposition rate. The highest Tc(R=0)'s of as-deposited films are 88K and 90K on (100) plane of MgO and (110) of $SrTiO_3$ respectively.

EFFECTS OF N_2O ON PREPARATION OF $Ba_2YCu_3O_X$ FILMS BY EXCIMER LASER ABLATION WITH LASER IRRADIATION ON GROWING SURFACE

Toshiharu Minamikawa*,Yasuto Yonezawa*,Shigeru Otsubo**,Toshihiro Maeda**
Akiharu Morimoto**,Tatsuo Shimizu**
*Industrial Reseach Institute of Ishikawa,Kanazawa,920-02,Japan
**Department of Electronics,Faculty of Technology, Kanazawa University
Kanazawa,920,Japan

So far, we had reported low temperature preparation technique of $Ba_2YCu_3O_X$ superconducting films by ArF excimer laser ablation with O_2 environment. We had revealed that a laser irradiation onto the growing film surface improves the crystallinity, superconducting properties, and surface morphology for films on various substrates at relatively low substrate temperature.

In this study, the effect of N_2O instead of O_2 on preparation of superconducting flms was examined in a similar technique. The film deposition was carried out by the laser ablation of a target material($Ba_2YCu_3O_X$) in vacuum chamber with N_2O environment of 27 Pa using ArF excimer laser (193nm wavelength, 10ns pulse width, 5Hz repetition rate). As a result, it was revealed that N_2O environment enhances the c-axis orientation for the film on crystalline Si substrate, compared with O_2 environment. Moreover, it was revealed that the laser irradiation onto the growing film surface with N_2O environment decreases the room temperature resistivity of the film on (100)MgO (Ts = 550°C) substrate, suggesting an improvement of the superconducting property due to the laser irradiation.

EFFECTS OF OXYGEN PRESSURE DURING LASER DEPOSITION ON CRYSTAL ORIENTATION IN $YBa_2Cu_3O_{7-\delta}$ FILMS.

H.Izumi, K.Ohata, T.Hase, K.Suzuki, and T.Morishita
Superconductivity Research Laboratory, ISTEC, Tokyo, Japan

In this study we present crystal orientation of the films deposited in the various pressures of oxygen gas ambient. ArF excimer laser pulses of 193nm and 10ns duration were used for ablation. The target was a 30-mm-diam sintered cylinder of a high-purity $YBa_2Cu_3O_{7-\delta}$. $SrTiO_3$ (100) substrates held at 700°C were used. The distance between the substrate and the target was fixed at 50mm. Experiments were carried out in the oxygen partial pressures of 10^{-5}-5Torr. The deposited films were cooled in the oxygen gas ambient of 300Torr. The films deposited in the pressures of less than 0.1Torr were grown with the c-axis normal to the film. The film prepared in 0.2Torr was a-axis oriented. The laser plume indeed didn't reached to the substrate in this pressure. The critical temperature was almost same for both around 90K, whereas, the resistivity at the onset was 2mΩ·cm and 0.2mΩ·cm, respectively. It is thought that this difference comes from the anisotropy of this system.

It is generally expected that the well oxidized films can be deposited in a higher oxygen pressure conditions. The crystalline structure of the films in higher pressures than 0.5Torr, however, were poor and no film was deposited in 5Torr. Some kind of the activation technique might be needed to synthesize a high quality film under such high pressure conditions.

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CHARACTERIZATION OF OXIDE SUPERCONDUCTING FILMS PREPARED BY PYROLYSIS OF ORGANIC ACID SALTS

M.Fujioka T.Seki T.Ohhashi S.Sawada K.Yamaguchi*

Nippon Mining Isohara Plant Kitaibaraki JAPAN
Nikko CS Chemical Hitachi Plant Hitachi JAPAN

Among the many film preparation techniques proposed for high T_c oxide superconductors, less attention is given to pyrolysis, but it is as important as others, since it is simple, less costly, and easy to apply to large area. This paper presents the film preparation technique by the pyrolysis of organic acid salts and resultant properties of film obtained in Y-Ba-Cu-O and Bi-Sr-Ca-Pb-Cu-O systems.

Octylic acid salts of Y, Ba, Cu, Bi, Sr and Ca, and naphthenic salts of Pb solved in xylene and toluen were mixed in proportion, and then coated on sintered YSZ or MgO substrates, which was followed by decomposing for 10 minutes at 500 °C. These treatments were repeated until desired film thickness was achieved. Coated substrates were then given RHQ treatment (1030 to 1050 °C, 30 to 180 sec.), and annealing for 1 to 150 hours at 700 to 870 °C for Bi system, or 30 minuets to 5 hours at 800 to 1000 °C.

In Bi system, the highest Tc obtained was 103 °K, and X-ray diffraction analysis showed that 2212 + 2223 structure was obtained. In Y system 123 structure was obtained, and the highest Tc was 80 °K. The effect of RHQ treatment was found to be the improvement in superconducting properties through the change in the grain morphology of the film.

PREPARATION OF SUPERCONDUCTING $Ba_2YCu_3O_{7-\delta}$ THIN FILMS BY THE DIPPING-PYROLYSIS PROCESS USING METAL NAPHTHENATES AND ACETYLACETONATES

Toshiya KUMAGAI, Takaaki MANABE, Wakichi KONDO, Hiroshi YOTOTA*, Hidehiro MINAMIUE** and Susumu MIZUTA

National Chemical Laboratory for Industry, Tsukuba 305, Japan

*Ebara Corp., Tokyo 144, Japan

**Nihon Kagaku Sangyo Co., Tokyo 110, Japan

Thin films of superconductor $Ba_2YCu_3O_{7-\delta}$ (BYCO) were prepared on the yttria-stabilized zirconia (YSZ) substrates by the dipping-pyrolysis process using metal naphthenates and acetylacetonates as starting materials. Barium, yttrium and copper naphthenates and acetylacetonates, with molar ratios of (A) Ba:Y:Cu = 2:1:3 and (B) 3:1:4.3, were dissolved in toluene and a mixture of pyridine and propionic acid, respectively, to make homogeneous solutions. Thermal analysis (TG-DTA) results of these solutions indicate that pyrolysis was completed in a narrower temperature range and weight loss after removal of solvent was smaller in the acetylacetonate system than the naphthenate system. After dipping, drying and preheating at 500°C were repeated 10-20 times, final heat treatment at 950°-970°C in O_2 gave 5-10 μm thick BYCO films, which showed superconduction at Tc,zero of 89-91 K. Results of scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis showed dense textures of orthorhombic BYCO grains.

The reaction between films and YSZ substrates during the above BYCO film preparation was also investigated by ICP-AES, SEM and XRD analyses. The reaction resulted in the formation of $BaZrO_3$ inside the substrates. Their reactivity increased (1) as the atmosphere was changed as: Ar< O_2 < air, and (2) as the reaction temperature was raised. With the heat treatment above 900°C in air or O_2, the formation of $BaZrO_3$ caused the depletion of Ba in the films, giving rise to the changes in film phases on the substrates as: BYCO→ BaY_2CuO_5 +CuO→ $Y_2Cu_2O_5$ +CuO.

A NEW FABRICATION METHOD OF MONOLITHIC LATERAL S-I-S STRUCTURE FROM AMORPHOUS Bi-O/Sr-Ca-Cu-O LAYER

T. Usuki, I. Yasui, Y. Yoshisato and S. Nakano

Functional Materials Research Center, SANYO Electric Co., Ltd.

Hirakata, Osaka, 573 Japan

A new fabrication method of monolithic lateral Superconductor-Insulator-Superconductor (SIS) structure was developed using a crystallization process of oxide superconductors. Oxide superconductors have different characteristics: superconducting, semiconducting and insulating, by controlling their composition. A superconducting Bi-Sr-Ca-Cu-O (BSCCO) area and a nonsuperconducting Sr-Ca-Cu-O (SCCO) area can be obtained on the same surface of the substrate by using this method.

The procedure is as follows. SCCO films were fabricated on an MgO single crystal substrate by an rf planer magnetron sputtering with a $Sr_1Ca_1Cu_2O_x$ target. The patterned Bi-O films were deposited on the as-deposited SCCO films by an electron beam evaporation method. Then the films were annealed at 870 C and above in air. The Bi-O films were diffused into the SCCO film to be crystallized to the BSCCO films. The X-ray diffraction analysis indicates that the obtained BSCCO films are mainly composed of high-Tc phase with high crystallinity of c-axis preferred orientation. These films, with a 0.15 μm thickness, show that the highest zero resistance Tc is 109 K. The SCCO films show semiconductor-like temperature dependence of resistivity.

Lateral or planer BSCCO/SCCO/BSCCO structures can be obtained by the use of fine patterned Bi-O films. We can attain good interface for the heterojunction of oxide-superconductor/oxide-semiconductor by using this method.

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Growth and Property of High-Tc Phase in Sputtered Bi(Pb)-Sr-Ca-Cu-O Thin Films

K.Haeda , .Iwamitsu, T.Kitamura, H.Kobayashi, T.Hasegawa, T.Shiono
Showa Electric Wire & Cable CO, LTD , Kawasaki , Japan
H.Kato, H.Yamamoto, M.Tanaka
College of Sci.& Technol.Nihon University , Funabashi , Japan

There are several superconducting phases in a Bi system corresponding to the number of Cu-O planes. The purpose of this work is to investigate a noble technique for a synthesis of a high-Tc Phase on MgO(100) plane. We examined to develop heat treatment techniques for amorphous Bi(Pb)-Sr-Ca-Cu-O thin films. The film composition was regulated to Bi:Sr:Ca:Cu=2:2:2:3 by adjusting a target composition and sputtering conditions. An important condition for growth of high-Tc Phase was to keep the stoichiometry during anneal. For the purpose to satisfy such the condition, it was effective to do a heat treatment putting a MgO plate on the film surface. By this method, a preferential growth of the high-Tc Phase took place even for thirty minutes at the reduced pressure of oxygen.
As a result, the film which contained the high-Tc Phase above 70% was prepared, and it revealed the Tc of zero resistance of about 105K.

FOCUSED ION BEAM PROCESSES FOR Bi-Ca-Sr-Cu-O SUPERCONDUCTING THIN FILMS

S. FUJIWARA, R. YUASA, H. KUWAHARA, M. NAKAO, and S. SUZUKI
SANYO Tsukuba Research Center, Tsukuba, Ibaraki, Japan

Focused Ion Beam (FIB) has been expected as a promising tool for microfabrication of semiconductor devices with a submicron dimension. FIB can be also a useful technique for patterning or modification of high-Tc superconducting thin films. Some patterning processes for superconducting films using maskless-etching with Au^+ or Ga^+ FIB have been reported. Devices such as DC-SQUID's are fabricated successfully.

We demonstrate FIB processes with Bi^+ ions which we used to pattern Bi-Ca-Sr-Cu-O thin films and to fabricate planer S-N-S junctions. These processes involve no wet-process and have no regard for the problem of impurities. Therefore, it is expected that the films are patterned with little degradations of the film properties. V-shaped fine grooves with the 0.3μm width and the depth of 1.5μm were obtained by the sputter-etching using 100keV Bi^+ FIB and metal or semiconductor were deposited into the grooves to fabricate the junctions Characteristics of the planer S-N-S junctions will be also discussed.

OBSERVATION OF BOUNDARY LAYER OF OXIDE SUPERCONDUCTING FILMS PASTED ON VARIOUS SUBSTRATE

S. Fuchino, K. Agatsuma, T. Ohara, H. Tateishi and K. Kaiho

Electrotechnical Laboratory
1-1-4 Umezono, Tsukuba, Ibaraki, 305 JAPAN

All the reported thin film growth techniques have required a post annealing or a heating of the substrate during the deposition.

In this paper the influence of these annealing to the substrate and oxide superconducting films has been investigated by means of energy dispersive X-ray (EDX) analysis and scanning electron microscopy(SEM) examinations in order to get the basic information of the substrate to be proposed for Y-Ba-Cu-O(YBCO) and Ba-Sr-Ca-Cu-O(BSCCO) films which will be adopted for future superconducting devices. To enhance these influences, relatively thin films of YBCO and BSCCO pasted on various substrate(MgO, $SrTiO_3$, Al_2O_3, Y 8% stabilized ZrO_2(YSZ), etc.)rather than sputtered thin films have been chosen.

The results show the boundary layer of the intermediate products which consist of Ba compounds between the YBCO layer and substrate and also Sr and Bi compounds between the BSCCO layer and substrate. Considering the thickness of the boundary layer of the intermediate products, MgO substrate might be recommended for YBCO films and $SrTiO_3$ substrate might be recommended for BSCCO films.

LOW NOISE OPERATION OF NOVEL MAGNETIC SENSOR USING CERAMIC HIGH Tc SUPERCONDUCTOR FILM

H. Shintaku, H. Nojima, M. Nagata, E. Ohno and M. Koba
Sharp Corporation, Central Research Laboratories,
2613-1 Ichinomoto-cho, Tenri,
Nara 632
JAPAN

We report the low noise operation of a magnetic sensor employing magnetoresistive effect of ceramic high Tc superconductor films. $Y_1Ba_2Cu_3O_{7-x}$ ceramic superconductor film prepared by a spray pyrolysis method was patterned to a meander shape. The film element was mounted in a package with dry N_2 gas to prevent from degradation by a reaction with atmospheric moisture. Dependence of the voltage noise of the element on a direction of the field and on a magnitude of a current through the element was measured systematically. The magnetic field resolution of 2×10^{-6} gauss/$(Hz)^{1/2}$ at 100 Hz was obtained on the basis of the noise characteristics. By applying a modulation of a.c. bias field, the external magnetic field was detected with Lock-in-Amplifier. As a result, the field detection was performed with low noise. Furthermore, it is demonstrated that a stability for more than 1 year was confirmed.

DESIGN AND FABRICATION OF SINGLE-LEVEL DC-SQUID MAGNETOMETERS MADE OF Bi-Sr-Ca-Cu OXIDE FILMS

M. Matsuda, Y. Murayama, H. Shinozuka*, T. Sawada**, M. Koyanagi, M. Nakanishi, N. Kasai, and T. Endo

Electrotechnical Laboratory, Tsukuba, Japan
* Science University of Tokyo, Tokyo, Japan
**Chiba Institute of Technology, Narashino, Japan

We report on the design and fabrication of all high-T_C dc-SQUID magnetometers made of Bi-Sr-Ca-Cu oxide films.

Bi-Sr-Ca-Cu oxide films were deposited by rf magnetron sputtering in a mixture of 20% O_2 and Ar gas onto (100) MgO substrates at about 740°C. The films annealed at about 870°C have zero resistance temperature around 70K.

In applying such high-T_C oxide films to integrated dc-SQUID magnetometers consisting of the flux coupling system to the SQUID loop, single-level structure is desirable to avoid crossings of lines and superconductive contacts. We have patterned a dc-SQUID loop having two parallel microbridges, a pick-up loop and a modulation (feedback) loop in the same level from a single layer of oxide film by an etching process. A SQUID loop and pick-up loop are connected directly in parallel. The small SQUID loop is electrically coupled to the outer pick-up loop being sensitive to the magnetic field. The inductance seen by the microbridges is determined mainly by the inductance of the inner SQUID loop (L_S). Since the inductance of the SQUID loop is smaller than that of the pick-up loop (L_P), coupling loss, roughly given by $\{1-(L_S/L_P)\}$, must be accepted.

Details of the design and fabrication of the integrated dc-SQUIDs will be described.

APPLICATION OF HIGH T_c SUPERCONDUCTING THICK FILM TO SUPERCONDUCTING INTERCONNECTION AND CONTACT

K.Hatanaka, M.Kaitou*, Y.Matsuzaki*, M.Toyokawa**, S.Kashu* and C.Hayashi
ULVAC JAPAN, Ltd., 2500 Hagisono, Chigasaki 253, JAPAN
*Vacuum Metallurgical Co., Ltd., 516 Yokota, Sanbu 289-12, JAPAN
**Tohoku Vacuum Metallurgical Co., Ltd., Ichikawa, Hachinohe 031, JAPAN

Line shaped superconducting thick films, approximately 1 mm width and 10 μm thick, have been formed on a MgO substrate by gas deposition of fine powder. Y-Ba-Cu-O, Ag doped Y-Ba-Cu-O, Bi-Pb-Sr-Ca-Cu-O, and layered Pb/Bi-Sr-Ca-Cu-O films are successfully made and all films showed superconductivity above 70 K. For best sample of layered Pb/Bi-Sr-Ca-Cu-O film, T_c=104 K and J_c=225 A/cm^2 at 77 K in zero field. This deposition system are utilized as a maskless patterning method for superconducting interconnection between contacts on high T_c superconducting devices. The measured contact resistance between base electrode film and overlaid interconnecting film, both made of high Tc material, are 1.2 mΩ cm^2 for YBCO/YBCO, 4.8 mΩ cm^2 for BPSCCO/BPSCCO and 0.13 m Ωcm^2 for (Pb/BSCCO)/(Pb/BSCCO) at 100K and all contacts become superconducting below 60 K. Best critical current density at contact is 175 A/cm^2 (T= 4.2 K) for YBCO/YBCO contact.

GAPLESS CHARACTERISTICS OF SUPERCONDUCTIVITY IN SURFACE LAYER OF HTSC

N.Yoshikawa, T.Murakami and M.Sugahara
Faculty of Engineering, Yokohama National University
Hodogaya, Yokohama, 240, Japan

The surface layer of High-Tc oxide superconductor has deterioated superconductivity due to the lack of some element and/or imperfect morphology. The deteriorated surfaces are believed to cause difficulties to get ideal performance in tunnel junctions and high frequency transmission lines. In this report we make theoretical study of the high frequency loss characteristics of the surface layer of oxide superconductors based on the proximity effect theory. It is supposed that the layer itself is in normal state, and that it has superconductivity by way of the proximity effect. The calculated state density is compared with the data observed in tunnel experiment. Using the obtained pair-breaking perturbation parameter, the surface impedance is calculated after the theory of Mattis-Bardeen. The result are compared with recent experimental data on absorption of microwave in oxide superconducting films.

JOSEPHSON EFFECT IN EPITAXIAL $Ba_2YCu_3O_x$ THIN FILMS ON ZrO_2/Si

Hiroaki Myoren, Yukio Nishiyama, Naokazu Miyamoto, Yukio Osaka and Toshihiko Hamasaki*

Department of Electrical Engineering, Faculty of Engineering, Hiroshima University, Saijo, Higashi-Hiroshima 724, Japan
*ULSI Research Center, Toshiba Corporation, 1 Komukai Toshiba-Cho, Saiwai-ku, Kawasaki 210, Japan

For fabricating the microbridge type Josephson junction, it is necessary to develop appropriate microfabrication technique. The films on oxide substrates such as $SrTiO_3$ or MgO have been patterned mainly by wet etching and laser etching, which are not easy to use for making fine patterns. Fortunately, the established VLSI technology based on Si have the appropriate microfabrication technique. Furthermore, in previous papers, we reported on the successful as-grown preparation of the epitaxially grown $Ba_2YCu_3O_x$ thin films on Si substrate with epitaxially grown ZrO_2 as a buffer layer and the Tc(end) of these films exceeded liquid nitrogen temperature.

Using the silicon substrates patterned with the trench, the superconducting microbridge junctions have been fabricated in as-grown $Ba_2YCu_3O_x$ thin films by rf-magnetron sputtering. The microbridge junctions with constrictions as small as submicron dimension were obtained. I-V characteristics of the microbridges sometimes consist of nearly linear sections with an overall parabolic behavior and this result means that these I-V characteristics seem to be dominated by a vortex motion. These microbridge junctions behaved as Josephson junction and were observed microwave-induced steps. Based on Likharev's theory, it is suggested that these devices show Josephson effect in the Abrikosov vortex motion region.

DETECTION OF 6 KEV X-RAYS BY USING LARGE-SIZE Nb-BASED TUNNEL JUNCTIONS

K. Ishibashi, K. Takeno, K. Mori, T. Sakae, Y. Matsumoto, A. Katase
S. Takada,* H. Nakagawa,* M. Aoyagi,* H. Akoh,* and S. Kohjiro*
Kyushu University, Fukuoka, Japan
*Electrotechnical Laboratory, Tsukuba, Japan

In nuclear radiation detection, superconductors have the inherent advantage of better energy resolution than that of semiconductors. Since Nb is a refractory material, Nb-based tunnel junctions are resistant against the thermal cycle from room to cryogenic temperature. This property is of great importance to the practical use of the tunnel junctions as radiation detectors. Lithographic technique has recently been developed for fabricating Josephson LSI circuits. In this study, the technique has been employed to produce Nb/Al/AlOx/Nb tunnel junctions for high-resolution x-ray detection. The leakage current was suppressed to an admissible level. The junctions having the size of as large as 100 μm successfuly detected 6 keV x rays.

ALL HIGH-Tc OXIDE SUPERCONDUCTOR JUNCTION USING Bi-Sr-Ca-Cu-O THIN FILMS

K.MIZUNO, H.HIGASHINO, K.SETSUNE, and K.WASA

Central Research Labolatories, Matsushita Electric Industrial Co.Ltd., Moriguchi, Osaka 570, Japan

It is much attractive to realize a sandwich-type junction device using a high-Tc oxide superconductor because of its potential for high temperature operation and controllability of its characteristics. In a fabrication of these junctions, deposition techniques or materials of barrier layer must be carefully selected to avoid interdiffusion between each layer. Recently, we have succeeded in the fabrication of a Bi-Sr-Ca-Cu-O(2212)/Bi-Sr-Cu-O(2201)/Bi-Sr-Ca-Cu-O(2212) junction. This is, in our knowledge, the first report of the thin film type Josephson junction using all Bi-based compound oxide superconductors.

Each layer was deposited successively on MgO(100) substrate which was heated at about 650^{o}C. The thickness of films were 300nm(base electrode),60nm, and 200nm(counter electrode), respectively. Both base electrode layer (2212) and barrier layer (2201) were identified to have c-axis oriented crystallinity from X ray diffraction analysis. The junction of 20X40 μm^2 in area was cut out from this multi-layered film using photolithography and Ar ion milling techniques. The critical temperature(Tc) of junction was about 50K, and its critical current was 2mA at 4.2K. We observed S/N/S type I-V characteristic under Tc and also observed some clear Shapiro steps induced by rf radiation. It can't be denied that there may be some micro shorts in our junction, however the thickness of barrier layer was rather thick, so we believe that this device is operated as S/N/S type Josephson junction, not micro shorts.

PRELIMINARY STUDY OF YBCO/Au/YBCO JOSEPHSON JUNCTION

S.Tanaka, H.Itozaki and S.Yazu

Itami Research Laboratories, Sumitomo Electric Ind., Ltd.

1-1 Koyakita 1-Chome, Itami, Hyogo, 664, Japan

We have grown a Y1Ba2Cu3Ox(YBCO)/Au/Y1Ba2Cu3Ox(YBCO) tri-layered structure using RF magnetron sputtering for YBCO and high vacuum evaporation for the Au barrier. We tried to fabricate an SNS junction with an area of 90um x 90um by using a tri-layered thin film through the "Whole-wafer" process. The structure of the device is shown in Fig 1. X-ray Diffraction analysis revealed a strong c-axis orientation of the YBCO thin film, even on the Au barrier. We observed critical current of the junction when the thickness of the Au barrier was less than 60nm. After applying microwave radiation of 8.96GHz to the junction, the critical current was suppressed from 0.31 to 0.18mA. Also, weak induced voltage steps in the I-V curve were observed. We think the most part of the suppression is caused by bolometric effect. However, these steps suggest that an ac-Josephson effect might occur in this device and that small part of the junction acts as a Josephson junction. The possibility of a micro-short between both YBCO layers still remains. However, We think these results encourage us to apply high Tc materials to electronic devices.

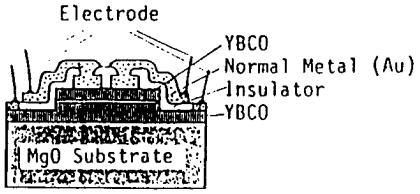

Fig.1

FABRICATION OF YBCO/BARRIER/YBCO STRUCTURE JUNCTIONS

Toshiyuki Matsui, Gensoh Matsubara*, Akiyoshi Nakayama**, Noritada Sato, Kazuo Mukae, and Yoichi Okabe*

Fuji Electric Co. R and D Ltd., Nagasaka, Yokosuka 240-01, Japan
*Department of Electronic Engineering, Faculty of Engineering, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan
**Department of Electrical Engineering, Faculty of Engineering, Kanagawa University, Kanagawa-ku, Yokohama 221, Japan

This report concerns with the morphology of the barrier layers and the characteristics of YBCO/barrier/YBCO junctions. An rf magnetron sputtering system was used to prepare these junctions. The substrate temperatures were 620°C for the lower YBCO, 470°C for the barrier layer, and 600°C for the upper YBCO. In this condition, the critical temperature for both the lower YBCO and the upper one were 60 K.

$SrTiO_3$ was used as the barrier layer in order to obtain the upper YBCO epitaxially. However, because $SrTiO_3$ was deposited in the form of crystal grains on the lower YBCO, many parts of the upper YBCO were deposited on the lower YBCO directly. It means that by increasing the barrier thickness the current passes were decreased. Even though the thickness of the barrier layer was up to 0.33 μm, the superconducting current was obtained. The I-V characteristics curve presented the periodic steps of 4 mV width. It seems that this phenomenon results of the morphology of the barrier layer. Assuming that this is caused by the charging effect, the capacitance is estimated in 4×10^{-17} F

STUDY OF VERTICAL TRANSPORTATION SYSTEM USING BY SUPERCONDUCTING LINEAR MOTOR

H.Nagano : University of Toyama. Toyama Japan
M.Kinugasa, T.Tokizawa : Power Reactor And Nuclear Fuel Development Corporation. Tokyo Japan
K.Hayakawa, K.Sasaki : Mitsubishi Heavy Industries, Ltd. Kobe Japan

A basic experimental equipment of a linear motor using by superconducting magnet was constructed and an experiment was made in order to investigate whether a linear motor method can be used for a vertical transportation equipment or not.
It is constituted by a transportation capsule which was made by FRP and in which liquid helium is saved, a superconducting magnet which is in a bottom of a capsule, normalconducting magnets which are around a capsule guide, and electric power supplies for magnets.
As a result of the experiment, it is found 30 kg of maximum thrust force can be get and the capsule floats still. And it is clear that calculated value and experimental one are almost same.
It can be concluded that the linear motor method is quite feasible although threr have been so far few reports of the construction of such facility capable of transporting massive and weight materials vertically.

FEASIBILITY STUDY OF COMPACT HIGH-Tc SUPERCONDUCTING CABLES BY BEAN MODEL FOR URBAN POWER SYSTEM

Tsukushi Hara Kiyoshi Okaniwa Takahiko Yamamoto
Engineering Research Center, Tokyo Electric Power Company
Tokyo, Japan

It becomes difficult and high in cost to construct new ducts for power transmission cables in dense underground region of urban area. In this presentation, feasibility study of compact high-Tc superconducting (HTSC) cables which should be applied to existing ducts (diameter:150mm) without the construction of new ducts is conducted. The following items has become clear.

(1)The future model system with the merit for HTSC cables is conceived.

(2)The necessity of flowing the superconducting current in the inner part of superconductor because of low Hc1 less than 100G is indicated, and it becomes clear by the measurement of hysteresis curve that the current flow in the superconductor roughly obeys Bean model.

(3)The design procedure of compact HTSC cable by Bean model is developed, and the conceptual design of HTSC cables for the model system is conducted. As a result, it becomes clear that Jc as $1x10^{5-6}$ A/cm^2 at 0.1-0.2T is necessary for the 66kV, 1000MVA HTSC cable which diameter is 130mm.

(4)There is no problem of the model system for the voltage stability, short circuit current, power stability, and so on by the system analysis.

(5)About 30% cost reduction of the HTSC cable model system is estimated compared with the normal-conducting cable model system.

DESIGN STUDY OF A 100KWH SMES

T. Nakano, K. Hayakawa : Mitsubishi Heavy Industries, Ltd. Kobe

Superconducting Magnetic Energy Strage (SMES) is very proper method for saving energy, because of its high efficiency and quick response.

We had designed a utility scale SMES (5 GWh) and set up a basic specification. On developing a utility scale SMES, it is necessary to scale up the size successively from prototype, demonstrational type, to utilitarian type. In this report, we report on the conceptual design for 100 kWh toroidal SMES as a prototype plant, magnetic field, electro-magnetic force, superconductor, cryostat, thermal insulating support, cooling system, and so on.

DESIGN STUDIES OF THE 20MWh TOROIDAL SMES MAGNET SYSTEM

Y.Sanada*,S.Akita**,T.Shintomi*** and T.Tanaka**
Research Association of Superconducting Magnetic Energy Storage
* Toshiba Corporation
** Central Research Institute of Electric Power Industry
*** National Laboratory for High Energy Physics

The present paper describes the design studies of the 20 MWh toroidal SMES magnet systems performed at the Research Association of Superconducting Magnetic Energy Storage.

The 20MWh SMES plant has a sufficient capacity for the power network stabilizing and for load-leveling in local area. In this design studies, toroidal coil system was assumed because of lower fringe field as compared with that of solenoidal coil system, and two coil systems were studied as a function of coil aspect ratio(minor radius/major radius) in order to look for the cost optimization. In both magnet systems, the magnet consists of 100 toroidal coils composed of full stabilized Nb3Sn/Al conductor which has a maximum operating current of 50 kA.

(1) In case of coil aspect ratio = 0.1
The toroidal coil has a minor radius of 3.6 m and maximum field of 6.8 T. The toroidal major radius is 36 m.

(2) In case of coil aspect ratio = 0.2
The toroidal coil has a minor radius of 4.5 m and maximum field of 5.3 T. The toroidal major radius is 22.5 m.

QUENCH PROTECTION STUDIES IN 20MWh SOLENOIDAL SMES MAGNET

T.Ishihara(1),T.Doi(1),T.Shintomi(2),T.Tanaka(3)

Research Association of Superconducting Magnetic Energy Storage
———— (1)IHI,(2)KEK,(3)CRIEPI

We present a basic analysis of a quench protection of 60m X5.04m^{H} solenoidal SMES magnet. This magnet generates a peak field of 7.5T at the end of the coil on energizing it to the operation current of 200kA. The conducter which is an aluminum stabilized cable of Nb_3Sn has been designed according to the fully stabilizing concept. We assume that the quench occurs in case of the conductor degraded or heated up by vacuum failure. We investigated the quenching process of this magnet by numerical analysis and studied the protection scheme to dumping down the coolant and heating up the several parts of the coil.

- END -

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